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A MANUAL

OF

PHOTOGRAPHIC CHEMISTRY.

A MANUAL

OF

PHOTOGRAPHIC CHEMISTRY,

INCLUDING THE

PRACTICE OF THE COLLODION PROCESS.

BY

T. FREDERICK HARDWICH,

LATE DEMONSTRATOR OF CHEMISTRY AND LECTURER ON PHOTOGRAPHY
IN KING'S COLLEGE, LONDON.

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PREFACE TO THE SIXTH EDITION.

IN preparing a new Edition of his Work, the Author finds it growing under his hands in a way not originally anticipated. The only apology he can offer, is that he hears the 'Manual' spoken of as being useful for reference rather than for continuous perusal, and if so, each Part, and also each separate Chapter, ought to be as nearly as possible complete in itself, even at the expense of some repetition. In furtherance of this object, the employment of type of two sizes has been adopted, which will enable the reader to distinguish the elementary parts of the Work from those which, being more elaborate and minute, may be consulted only on occasion.

The Third Chapter, treating of latent images, has undergone some alteration in this Edition, and the Author having definitively adopted a particular hypothesis has given it that prominence which it appears to him to deserve.

With reference to Collodion, he believes that every statement which he makes concerning it may be implicitly received, since his opportunities of fixing correct data have been unusually great. At the same time he wishes it to be understood that he has now relinquished the commercial manufacture of Collodion, and that for the future no responsibility will attach to him.

Photographic printing has reached a point beyond which any further advance will be difficult. The Chapters relating to this subject have been once more re-arranged, but it is not anticipated that such a proceeding will again be necessary unless our present modes should be superseded.

Dry Collodion photography is in this Edition placed in the first or theoretical, as well as in the second or practical part of the Work. Major Russell has communicated an improved method, of the utility of which high expectations are entertained.

In conclusion, the Writer desires to thank those kind friends who have assisted him in collecting materials for this Edition, and to acknowledge his obligations to the authors of papers published during the past two years. His aim throughout has been to show strict impartiality in recording the results of his fellow-labourers, and if he has failed in doing so, the fault was not in the intention.

London, January 1*st,* 1861.

PREFACE TO THE THIRD EDITION.

It is a source of much gratification to the Author to find himself called upon to prepare a Third Edition of his Manual in less than fourteen months from the date of its first publication. No greater proof could have been afforded of the rapid advance which the Photographic Art is making in this Country.

On once more entering upon the task of revision, the Writer is led to reflect in what way the utility of the Work may be promoted; and from numerous inquiries he believes that this result will be attained by carefully omitting everything which does not possess *practical* as well as scientific interest. The majority of Photographers look to the Art to furnish them with amusement as well as instruction, and they are deterred from entering upon a study which seems to involve a great amount of technical detail.

The present Edition differs in many important particulars from those which preceded it. It has undergone a fresh arrangement throughout. In some parts it is condensed, in others enlarged. The Chapters on Photographic Printing are entirely re-written, and include the whole of the Author's investigations, as published in the Society's Journal. The minute directions given in this part of the Work will show that success in Photography is thought to depend very much upon a careful attention to minor particulars.

Another point which has been kept in view, is to recommend, as far as possible, the employment of chemicals which are used in medicine, and hence are vended by all druggists throughout the United Kingdom. It is often an advantage to the Amateur to be able to purchase his materials near at hand; and, if the common impurities of the commercial articles are pointed out, and directions given for their removal, the 'London Pharmacopœia' will be found to include almost all the chemicals necessary for the practice of the Art.

Great additions have been made to the Index of the present Edition, which is now so complete that a reference to it will at once point out the most important facts relating to each subject, and the different parts of the Work at which they are described.

In conclusion, a hope is expressed that this 'Manual of Photographic Chemistry' may be found to be a complete and trustworthy guide on every point connected with the theory and practice of the Collodion process.

London, June 2nd, 1856.

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A MANUAL

OF

PHOTOGRAPHIC CHEMISTRY.

INTRODUCTION.

In attempting to impart knowledge on any subject, it is not sufficient that the writer should himself be acquainted with that which he professes to teach. Even supposing such to be the case, yet much of the success of his effort must depend upon the manner in which the information is conveyed; for as, on the one hand, a system of extreme brevity always fails of its object, so, on the other, a mere compilation of facts imperfectly explained tends only to confuse the reader.

A middle course between these extremes is perhaps the best to adopt; that is, to make selection of certain fundamental points, and to explain them with some minuteness, leaving others of less importance to be dealt with in a more summary manner, or to be altogether omitted.

But independently of observations of this kind, applying to educational instruction in general, it may be remarked, that there are sometimes difficulties of a more formidable description to be overcome. For instance, in treating of a science, like Photography, which involves numerous and complex reactions, there is great danger of attributing effects to wrong causes! Perhaps none but he who has himself worked in the laboratory can estimate this point in its proper light. In an experiment where the quantities of material acted upon are infinitesimally small, and the chemical changes involved of a most refined and subtle description, it is soon discovered that the slightest variation in the usual conditions suffices to alter the result.

Nevertheless Photography is truly *a science*, governed by fixed laws; and hence, as our knowledge increases, we may fairly hope that uncertainty will cease, and the same precision be attained as that with which chemical operations are usually performed.

The intention of the author in writing this work, is to impart a thorough knowledge of what may be termed the "First Principles of Photography," that the amateur may arm himself with a theoretical acquaintance with the subject before proceeding to its practice. To assist this object, care will be taken to avoid needless complexity in the formulæ, and all ingredients will be omitted which are not proved to be useful.

The impurities of chemicals will be pointed out as far as possible, and special directions given for their removal.

Amongst the great variety of Photographic processes which have been devised, those only will be selected which are correct on theoretical grounds, and are found in practice to succeed.

As the work is addressed to one supposed to be unacquainted both with Chemistry and Photography, pains will be taken to avoid the employment of all technical terms of which an explanation has not previously been given.

A SKETCH OF THE MAIN DIVISIONS TO BE ADOPTED, WITH THE PRINCIPAL SUBJECT-MATTER OF EACH.

The title given to the Work is "A Manual of Photographic Chemistry," and it is proposed to include in it a familiar explanation of the nature of the various chemical agents employed in the Art of Photography, with the rationale of the manner in which they are thought to act.

The division adopted is threefold:—

PART I. enters minutely into the *theory* of Photographic processes; PART II. treats of the *practice* of Photography upon Collodion; PART III. embraces a simple statement of the main laws of Chemistry, with the principal properties of the various substances, elementary or compound, which are employed by Photographers.

PART I., or "the Science of Photography," includes a full description of the chemical action of light upon the Salts of Silver, with its application to artistic purposes; all mention of manipulatory details, and of quantities of ingredients, being, as a rule, omitted.

In this division of the Work will be found ten Chapters, the contents of which are as follows:—

Chapter I. is a sketch of the history of Photography, intended to convey a general notion of the origin and progress of the Art, without dwelling on minute particulars.

Chapter II. describes the Chemistry of the Salts of Silver employed by Photographers; their preparation and properties; the phenomena of the action of Light upon them, with experiments illustrating it.

Chapter III. leads us on to the formation of *an invisible image* upon a sensitive surface, with the development or bringing out to view of the same by means of chemical reagents. This point, being of elementary importance, is described carefully; the reduction of metallic oxides, the properties of the bodies employed to reduce, and the hypotheses which have been entertained on the nature of the Light's action, are all minutely explained.

Chapter IV. treats of the fixing of Photographic impressions, in order to render them indestructible by diffused light.

Chapter V. contains a sketch of the *Optics* of Photography—the decomposition of white Light into its elementary rays, the Photographic properties of the different colours, the refraction of Light, and construction of Lenses. In the last Section of this Chapter will be found a short sketch of the history and use of the Stereoscope.

Chapter VI. explains the chemistry of Pyroxyline, with its solution in Alcoholized Ether, or Collodion; also of the *Nitrate Bath*, in which the photographic plates are rendered sensitive to light.

Chapter VII. describes the classification of Collodion Photographs as Positives and Negatives, with the distinctive peculiarities of each, and the most approved modes of obtaining them.

Chapter VIII. contains the theory of the production of Positive Photographs upon paper. In this Chapter will be found an explanation of the complex chemical changes involved in printing Positives, with the precautions which are required to ensure the permanency of the finished proofs.

Chapter IX. is an epitome of all that is known of the dry Collodion and Collodion preservative processes; their history, and the scientific principles upon which they are founded.

Chapter X. is supplementary to the others, and a brief notice of it will suffice. It explains the theory of the Photographic processes of Daguerre and Talbot; especially noticing those points in which they may be contrasted with Photography upon Collodion, but omitting all description of manipulatory details, which if included would extend the Work beyond its proposed limits. Photo-lithography, lately improved and perfected, is also alluded to in this Chapter.

The title of the second principal division of the Work, viz. "The practice of Photography upon Collodion," explains itself. Attention however may be invited to the fourth Chapter, in which a classification is given of the principal imperfections in Photographs, with short directions for their removal.

In Part III. will be found a statement of the laws of chemical combination, and, in addition, a list of Photographic chemicals, alphabetically arranged, including their preparation and properties as far as required for their employment in the Art.

reader will at once gather from this sketch of the ts of the volume before him, that whilst the general of every Photographic process is described, with eparation and properties of the chemicals employed, directions in the minor points of manipulation are ted to Photography upon Collodion, that branch of t being the one to which the time and attention of thor have been especially directed. Collodion is al- by all to be a good vehicle for the sensitive Silver and successful results can be obtained with a very expenditure of time and trouble, if the solutions em- in the process are prepared in a state of purity.

CHAPTER I.

HISTORICAL SKETCH OF PHOTOGRAPHY.

The Art of Photography, which has now attained such perfection, and has become so popular amongst all classes, is one of comparatively recent introduction.

The word Photography means literally "writing by means of Light;" and it includes all processes by which any kind of picture can be obtained by the chemical agency of Light, without reference to the nature of the sensitive surface upon which it acts.

The philosophers of antiquity, although chemical changes due to the influence of Light were continually passing before their eyes, do not appear to have directed their attention to them. Some of the *Alchemists* indeed noticed the fact that a substance termed by them "Horn Silver," which was probably a Chloride of Silver which had undergone fusion, became *blackened* by exposure to Light; but their ideas on such subjects being of the most erroneous nature, nothing resulted from the discovery.

The first philosophical examination of the decomposing action of Light upon compounds containing Silver was made by the illustrious Scheele, no longer than three-quarters of a century ago, viz. in 1777. It was also remarked by him that some of the coloured rays of Light were peculiarly active in promoting the change.

Earliest application of these facts to purposes of Art.— The first attempts to render the blackening of Silver Salts by Light available for artistic purposes were made by

Wedgwood and Davy about A.D. 1802. A sheet of white paper or of white leather was saturated with a solution of Nitrate of Silver, and the *shadow* of the figure intended to be copied projected upon it. Under these circumstances the part on which the shadow fell remained white, whilst the surrounding exposed parts gradually darkened under the influence of the sun's rays.

Unfortunately these and similar experiments, which appeared at the outset to promise well, were checked by the experimentalists being unable to discover any means of fixing the pictures, so as to render them indestructible by diffused Light. The unchanged Silver Salt being permitted to remain in the white portions of the paper, naturally caused the proofs to blacken in every part, unless carefully preserved in the dark.

Introduction of the Camera Obscura, and other Improvements in Photography.—The "Camera Obscura," or darkened chamber, by means of which a luminous image of an object may be formed, was invented by Baptista Porta, of Padua; but the preparations employed by Wedgwood were not sufficiently sensitive to be easily affected by the subdued light of that instrumeut.

In the year 1814, however, twelve years subsequent to the publication of Wedgwood's paper, M. Niépce, of Châlons, having directed his attention to the subject, succeeded in perfecting a process in which the Camera could be employed, although the sensibility was still so low that an exposure of some hours was required to produce the effect.

In the process of M. Niépce, which was termed "Heliography," or "sun-drawing," the use of the Silver Salts was discarded, and a resinous substance, known as "Bitumen of Judæa," substituted. This resin was smeared on the surface of a metal plate, and exposed to the luminous image. The light in acting upon it so changed its properties, that it became *insoluble* in certain essential oils. Hence, on subsequent treatment with the oleaginous solvent, the *shadows* dissolved away, and the *lights* were represented by the unaltered resin remaining on the plate.

The Discoveries of M. Daguerre.—MM. Niépce and Daguerre appear at one time to have been associated as partners, for the purpose of mutually prosecuting their researches; but it was not until after the death of the former, viz. in 1839, that the process named the Daguerreotype was given to the world. Daguerre was dissatisfied with the slowness of action of the Bitumen sensitive surface, and directed his attention mainly to the use of the Salts of Silver, which are thus again brought before our notice.

Even the earlier specimens of the Daguerreotype, although far inferior to those subsequently produced, possessed a beauty which had not been attained by any Photographs prior to that time.

The sensitive plates of Daguerre were prepared by exposing a silvered tablet to the action of the vapour of *Iodine*, so as to form a layer of Iodide of Silver upon the surface. By a short exposure in the Camera an effect was produced, not visible to the eye, but appearing when the plate was subjected to the vapour of Mercury. This feature, viz. the production of a *latent* image upon Iodide of Silver, with its subsequent development by a chemical reagent, is one of the first importance. Its discovery at once reduced the time of taking a picture from hours to minutes, and promoted the utility of the Art.

Daguerre also succeeded in *fixing* his proofs, by removal of the unaltered Iodide of Silver from the shadows. The processes employed however were imperfect, and the matter was not set at rest until the publication of a paper by Sir John Herschel, on the property possessed by "Hyposulphites" of dissolving the Salts of Silver insoluble in water.

On a means of Multiplying Photographic Impressions, and other Discoveries of Mr. Fox Talbot.—The first communication made to the Royal Society by Mr. Fox Talbot, in January, 1839, included only the preparation of a sensitive paper for copying objects by application. It was directed that the paper should be dipped first in solution of

Chloride of Sodium, and then in Nitrate of Silver. By proceeding in this way a white substance termed *Chloride of Silver* is formed, more sensitive to light than the Nitrate of Silver originally employed by Wedgwood and Davy. The object is laid in contact with the prepared paper, and, being exposed to light, a copy is obtained, which is *Negative,—id est,* with the light and shade reversed. A second sheet of paper is then prepared, and the first, or Negative impression, laid upon it, so as to allow the sun's light to pass through the transparent parts. Under these circumstances, when the Negative is raised, a natural representation of the object is found below; the tints having been again reversed by the second operation.

This production of a Negative Photograph, from which any number of Positive copies may be obtained, is a cardinal point in Mr. Talbot's invention, and one of great importance.

The patent issued for the process named *Talbotype* or *Calotype* dates from February, 1841. A sheet of paper is first coated with Iodide of Silver by soaking it alternately in Iodide of Potassium and Nitrate of Silver; it is then washed with solution of Gallic Acid, containing Nitrate of Silver (sometimes termed *Gallo-Nitrate of Silver*), by which the sensibility to light is greatly augmented. An exposure in the Camera of some seconds or minutes, according to the brightness of the light, impresses an invisible image, which is brought out by treating the plate with a fresh portion of the mixture of Gallic Acid and Nitrate of Silver employed in exciting.

On the use of Glass Plates to retain sensitive Films.—The principal defects in the Calotype process are attributable to the coarse and irregular structure of the fibre of paper, even when manufactured with the greatest care, and expressly for Photographic purposes. In consequence of this, the same amount of exquisite definition and sharpness of outline as that resulting from the use of metal plates, cannot be obtained.

We are indebted to Sir John Herschel for the first employment of glass plates to receive sensitive Photographic films.

The Iodide of Silver may be retained upon the glass by means of a layer of Albumen or white of egg, as proposed by M. Niépce de Saint-Victor, nephew to the original discoverer of the same name.

A more important improvement still was the employment of "Collodion" for a similar purpose.

Collodion is an ethereal solution of a substance almost identical with Gun-cotton. On evaporation it leaves a transparent layer, resembling goldbeater's skin, which adheres to the glass with some tenacity. M. Le Grey of Paris originally suggested that this substance might perhaps be rendered available in Photography, but our own countryman, the late Mr. Archer, was the first to carry out the idea practically. In a communication to 'The Chemist' in the autumn of 1851, this gentleman gave a description of the Collodion process much as it now stands; at the same time proposing the substitution of *Pyro*-gallic Acid for the Gallic Acid previously employed in developing the image.

At that period no idea could have been entertained of the stimulus which this discovery would render to the progress of the Art; but experience has now abundantly demonstrated, that, as far as all qualities most desirable in a Photographic process are concerned, none at present known can excel, or perhaps equal, the Collodion process.

CHAPTER II.

THE SALTS OF SILVER EMPLOYED IN PHOTOGRAPHY.

By the term of *Salt* of Silver we understand that the compound in question contains Silver, but not in its elementary form; the metal is in fact in a state of chemical union with other elements which disguise its physical properties, so that the Salt possesses none of the external characters of the Silver from which it was produced.

Silver is not the only metal which forms Salts; there are Salts of Lead, Copper, Iron, etc. *Sugar of Lead* is a familiar instance of a Salt of Lead. It is a white crystalline body, easily soluble in water, the solution possessing an intensely sweet taste; chemical tests prove that it contains Lead, although no suspicion of such a fact could be entertained from a consideration of its general properties.

Common Salt, or Chloride of Sodium, which is the type of the salts generally, is constituted in a similar manner; that is to say, it contains a metallic substance, the characters of which are masked, and lie hid in the compound.

The contents of this Chapter may be arranged in three Sections: the first describing the Chemistry of the Salts of Silver; the second, the action of Light upon them; the third, the preparation of a sensitive surface, with experiments illustrating the formation of the Photographic image.

SECTION I.

Chemistry of the Salts of Silver.

The principal Salts of Silver employed in the Photographic processes are four in number, viz. Nitrate of Silver, Chloride of Silver, Iodide of Silver, and Bromide of Silver. In addition to these, it will be necessary to describe the Oxides of Silver.

THE PREPARATION AND PROPERTIES OF THE NITRATE OF SILVER.

Nitrate of Silver is prepared by dissolving metallic Silver in Nitric Acid. Nitric Acid is a powerfully acid and corrosive substance, containing two elementary bodies united in definite proportions: these are Nitrogen and Oxygen; the latter being present in greatest quantity.

Nitric Acid is a powerful solvent for the metallic bodies generally. To illustrate its action in that particular, as contrasted with other acids, place pieces of silver-foil in two test-tubes, the one containing dilute Sulphuric, the other dilute Nitric Acid; on the application of heat a violent action soon commences in the latter, but the former is unaffected. In order to understand this, it must be borne in mind that when a metallic substance dissolves in an acid, the nature of the solution is different from that of an aqueous solution of salt or sugar. If salt water be boiled down until the whole of the water has evaporated, the salt is recovered with properties the same as at first; but if a similar experiment be made with a solution of Silver in Nitric Acid, the result is different: in that case we do not obtain *metallic* Silver on evaporation, but Silver *combined with Oxygen and Nitric Acid,* both of which are in a state of chemical combination with the metal.

If the effects produced by treating Silver with Nitric Acid be closely examined, we find them to be of the following nature:—first, a certain amount of Oxygen is imparted to the metal, so as to form an *Oxide;* then this Oxide dissolves in another portion of the Nitric Acid, producing *Nitrate* of the Oxide, or, as it is shortly termed, Nitrate of Silver.*

It is this *instability* of Nitric Acid—its proneness to part with Oxygen—which renders it superior to the Sulphuric and to most acids in dissolving Silver and various other substances, both organic and inorganic.

Properties of Nitrate of Silver.—In preparing Nitrate of Silver, when the metal is dissolved, the solution is boiled down and set aside to crystallize. The salt however as so obtained is still acid to test-paper, and requires either re-crystallization, or careful heating to about 300° Fahrenheit. It is this retention of small quantities of Nitric Acid, and other impurities, which renders much of the commercial Nitrate of Silver useless for Photography, until after a second crystallization.

Pure Nitrate of Silver occurs in the form of white crystalline plates, which are very heavy and dissolve readily in an equal weight of cold water. The solubility is much lessened by the presence of free Nitric Acid, and in the *concentrated* Nitric Acid the crystals are almost insoluble. Boiling Alcohol takes up about one-fourth part of its weight of the crystallized Nitrate, but deposits nearly the whole on cooling. Nitrate of Silver has an intensely bitter and nauseous taste; acting as a caustic, and corroding the skin by a prolonged application. Its aqueous solution does not redden blue litmus-paper; on the contrary, the pure re-crystallized and dried Nitrate of Silver restores the blue colour of paper previously reddened.

Heated in a crucible the salt melts, and when poured into a mould and solidified, forms the white *lunar caustic* of commerce. At a still higher temperature it is decomposed, and bubbles of Oxygen Gas are evolved: the melted mass cooled and dissolved in water leaves behind a black powder, and yields a solution, which contains Nitrite in addition to Nitrate of Silver.†

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* The preparation of Nitrate of Silver from the standard coin of the realm is described in Part III., Art. "Silver."

† Nitrite of Silver differs from the Nitrate in containing less Oxygen, and

THE CHEMISTRY OF THE CHLORIDES OF SILVER.

Preparation of Protochloride of Silver.—The ordinary white Chloride of Silver may be prepared in two ways,—by the direct action of Chlorine upon metallic Silver, and by double decomposition between two salts.

If a plate of polished silver be exposed to a current of Chlorine Gas* it becomes after a short time coated on the surface with a superficial film of white powder. This powder is Chloride of Silver, containing the two elements Chlorine and Silver united in single equivalents.

Preparation of Chloride of Silver by double decomposition.—In order to illustrate this, take a solution in water of Chloride of Sodium or "common salt," and mix it with a solution containing Nitrate of Silver; immediately a dense, curdy, white precipitate falls, which is the substance in question.

In this reaction the elements change places; the Chlorine leaves the Sodium with which it was previously combined, and crosses over to the Silver; the Oxygen and Nitric Acid are released from the Silver, and unite with the Sodium; thus

Chloride of Sodium *plus* Nitrate of Silver
equals Chloride of Silver *plus* Nitrate of Soda.

This interchange of elements is termed by chemists *double decomposition;* further illustrations of it, with the conditions necessary to the proper establishment of the process, are given in the first Chapter of Part III.

The essential requirements in two salts intended for the preparation of Chloride of Silver, arc simply that the first should contain Chlorine, the second Silver, and that both should be soluble in water; hence the Chloride of Potassium or Ammonium may be substituted for the Chloride of Sodium, and the Sulphate or Acetate for the Nitrate of Silver.

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is formed from it by the abstraction of two atoms of that element; it is described in the vocabulary, Part III.

* For the properties of the element "Chlorine," see the third division of the Work.

In preparing Chloride of Silver by double decomposition, the white clotty masses which first form must be washed repeatedly with water, in order to free them from soluble Nitrate of Soda, the other product of the change. When this is done, the salt is in a pure state, and may be dried, etc., in the usual way.

Properties of Chloride of Silver.—Chloride of Silver differs in appearance from the Nitrate of Silver. It is not usually crystalline, but forms a soft white powder resembling common chalk or whiting. It is tasteless and insoluble in water; unaffected by boiling with the strongest Nitric Acid, but sparingly dissolved by concentrated Hydrochloric Acid.

Ammonia dissolves Chloride of Silver freely, as do solutions of Hyposulphite of Soda and Cyanide of Potassium. Concentrated solutions of the Chloride, Iodide, and Bromide of Potassium, Sodium, and Ammonium, are likewise solvents of Chloride of Silver, but to a limited extent, as will be more fully shown in Chapter IV., when treating of the modes of fixing the Photographic proofs.

Dry Chloride of Silver carefully heated to redness fuses, and concretes on cooling into a tough and semitransparent substance, which has been termed *horn silver* or *luna cornea.*

Placed in contact with metallic Zinc or Iron acidified with dilute Sulphuric Acid, Chloride of Silver is reduced to the metallic state, the Chlorine passing to the other metal under the decomposing influence of the galvanic current which is established.

Preparation and Properties of Subchloride of Silver.—If a plate of polished Silver be dipped in solution of Perchloride of Iron, a *black stain* is produced, the Perchloride sinking to the state of a *Proto*-chloride of Iron, and losing a portion of Chlorine, which passes to the Silver and converts it superficially into a Subchloride of Silver.

This compound differs from the white Chloride of Silver in containing less Chlorine. Very little, however, is known either of its composition or properties, and no formula can be assigned to it. The only facts certainly ascertained with regard to the Subchloride of Silver are, that it is a pulverulent substance of a bluish-black colour, not easily affected by Nitric Acid, but decomposed by fixing agents, such as Ammonia, Hyposulphite of Soda, or Cyanide of Potassium, into Chloride of Silver, which dissolves, and insoluble metallic Silver.

THE CHEMISTRY OF IODIDE OF SILVER.

The properties of *Iodine* are described in the third division of the Work: they are analogous to those of Chlorine and Bromine, the Silver Salts formed by these elements bearing also a strong resemblance to each other.

Preparation and Properties of Iodide of Silver.—Iodide of Silver may be formed in an analogous manner to the Chloride, viz. by the direct action of the vapour of Iodine upon metallic Silver, or by double decomposition between solutions of Iodide of Potassium and Nitrate of Silver.

When prepared by the latter mode it forms an impalpable powder, the colour of which varies with the manner of precipitation. If the Iodide of Potassium be in excess, the Iodide of Silver falls to the bottom of the vessel nearly white; but with an excess of Nitrate of Silver it is of a straw-yellow tint. This point may be noticed, because the yellow salt is the one adapted for Photographic use, the other being insensible to the influence of Light.

Iodide of Silver is tasteless and inodorous: insoluble in water and in dilute Nitric Acid. It is scarcely dissolved by Ammonia, which serves to distinguish it from the Chloride of Silver, freely soluble in that liquid. Hyposulphite of Soda and Cyanide of Potassium both dissolve Iodide of Silver; it is also soluble in solutions of Bromide, and Iodide, of Potassium, Sodium, and Ammonium, as will be further explained in Chapter IV.

Iodide of Silver is reduced by Metallic Zinc in the same manner as the Chloride of Silver, forming soluble Iodide of Zinc and leaving a black powder.

THE PREPARATION AND PROPERTIES OF BROMIDE OF SILVER.

This substance so closely resembles the corresponding salts containing Chlorine and Iodine, that a short notice of it will suffice.

Bromide of Silver is prepared by exposing a silvered plate to the vapour of Bromine, or by adding solution of Bromide of Potassium to Nitrate of Silver. It is an insoluble substance, slightly yellow in colour, and distinguished from Iodide of Silver by dissolving in strong Ammonia and in Chloride of Ammonium. It is freely soluble in Hyposulphite of Soda and in Cyanide of Potassium.

The properties of the element Bromine are described in Part III.

CHEMISTRY OF THE OXIDES OF SILVER.

The Protoxide of Silver (AgO).—If a little Potash or Ammonia be added to solution of Nitrate of Silver, an olive-brown substance is formed, which, on standing, collects at the bottom of the vessel. This is Oxide of Silver, displaced from its previous state of combination with Nitric Acid by the stronger oxide, Potash. Oxide of Silver is soluble *to a very minute extent* in pure water, the solution possessing an alkaline reaction to Litmus; it is easily dissolved by Nitric or Acetic Acid, forming a neutral Nitrate or Acetate of Silver; also soluble in Ammonia (Ammonio-Nitrate of Silver), and in Nitrate of Ammonia, Hyposulphite of Soda, and Cyanide of Potassium.

The Suboxide of Silver (Ag_2O ?).—Rose has shown that when Protoxide of Iron is brought into contact with Protoxide of Silver under certain conditions, one-half of the oxygen contained in the latter oxide passes to the former, and an intensely black powder falls, consisting of Peroxide of Iron with *Sub*oxide of Silver. If strong acids are present in the above reaction, as for instance, when Sulphate of Protoxide of Iron is mixed with Nitrate of Silver, then no Suboxide is formed, but the Silver is deprived of the *whole* of its oxygen, in place of being only partially reduced.

Suboxide of Silver is a black powder which assumes the metallic lustre on rubbing, and when treated with acids is resolved into Protoxide of Silver, soluble in the acid, and insoluble Metallic Silver. Ammonia, Hyposulphite of Soda, and Cyanide of Potassium, likewise decompose Suboxide of Silver into Oxide of Silver and Metallic Silver. Suboxide of Silver possesses intense colouring powers, and a minute quantity shaken up with a large bulk of water renders the fluid inky black.

SECTION II.

On the Photographic Properties of the Salts of Silver.

In addition to the Salts of Silver described in the first Section of this Chapter there are many others well known to chemists, as the Acetate of Silver, the Sulphate, the Citrate of Silver, etc. Some occur in crystals which are soluble in water, whilst others are pulverulent and insoluble.

The Salts of Silver formed by colourless Acids are white when first prepared, and remain so if kept in a dark place; but they possess the remarkable peculiarity of being darkened by exposure to Light.

Action of Light upon the Nitrate of Silver.—The Nitrate of Silver is one of the most permanent of the Silver salts. It may be preserved unchanged in the crystalline form, or in solution in distilled water, for an indefinite length of time, even when constantly exposed to the diffused light of day. This is partly explained by the nature of the acid with which Oxide of Silver is associated in the Salt; *Nitric* Acid, possessing strong oxidizing properties, being opposed to the darkening influence of Light upon the Silver compounds.

Nitrate of Silver may, however, be rendered susceptible to the influence of Light, by adding to its solution *organic matter*, vegetable or animal. The phenomena produced in ıe are well illustrated by dipping a pledget of cotton- ›r a sheet of white paper, in solution of Nitrate of and exposing it to the direct rays of the sun; it darkens, until it becomes nearly black. The stains ıe skin produced by handling Nitrate of Silver are in the same way, and are seen most evidently when :t has been exposed to light.

varieties of organic matter which especially facilitate ckening of Nitrate of Silvèr are such as tend *to ab- xygen;* hence pure vegetable fibre, free from Chlo- ıuch, for instance, as the Swedish filtering-paper, is ıdered very sensitive by being simply brushed with n of the Nitrate, but a little grape sugar added soon ıines the decomposition.

›mposition of Chloride, Bromide, and Iodide of Silver ht.—Pure Chloride of Silver prepared in the moist ıanges slowly from white to *violet* on exposure to Bromide of Silver becomes of a grey colour, but is 'ected than the Chloride. Iodide of Silver (if free xcess of Nitrate of Silver) does not alter in appear- y exposure even to the sun's rays, but retains its tint unchanged. Of these three compounds there- *ıloride* of Silver is the most readily acted on by light, pers prepared with this salt will become far darker osure, than others coated with Bromide or Iodide of

·e are certain conditions which render the action of pon the Chloride of Silver more decided. These are, *ı excess of a soluble salt of Silver such as the Nitrate,* cond, *the presence of organic matter.* Pure Chloride ər would be useless as a Photographic agent, but a le with excess of Nitrate takes a strong impression. :odide of Silver, ordinarily unaffected, is blackened ıt when moistened with a solution of the Nitrate of

ınic matter combined with Chloride and Nitrate of gives a still higher degree of darkening in the solar d in this way the Photographic papers are prepared.

Action of Light upon organic compounds of Silver.—On adding diluted Albumen, or white of egg, to solution of Nitrate of Silver, a flocculent deposit forms which is a compound of the animal matter with Oxide of Silver, and is known as "Albuminate of Silver." This substance is at first white, but on exposure to light it assumes a brick-red colour.

Caseine, the animal principle of milk, is coagulated by Nitrate of Silver, the product behaving in the same manner as the Albuminate when exposed to light. Gelatine does not precipitate Nitrate of Silver: but if a sheet of transparent Gelatine be allowed to imbibe a solution of the Nitrate, it combines with it, and the product becomes of a clear ruby-red tint on exposure to light.

Many other organic compounds of Silver are darkened by light. The white Citrate of Silver changes to a red colour. Glycyrrhizin, the Sugar of Liquorice, also forms a white compound with Oxide of Silver which becomes brown or red in the sun's rays.

The photographic use of the organic Salts of Silver, and the extent to which they are affected by light, will be further considered in the eighth Chapter, when speaking of the theory of Positive printing.

SIMPLE EXPERIMENTS ILLUSTRATING THE ACTION OF LIGHT UPON A SENSITIVE LAYER OF CHLORIDE OF SILVER ON PAPER.

In the performance of the most simple experiments on the decomposition of Silver Salts by Light, the student may employ ordinary *test-tubes*, in which small quantities of the two liquids required for the double decomposition may be mixed together.

When however *concentrated* solutions are used in this way, the insoluble Silver Salt falls in dense and clotted masses, which, exposed to the sun's rays, quickly blacken on the exterior, but the inside is protected, and remains white. It is of importance therefore in Photography that the sensitive material should exist in the form of *a surface*, in order that the various particles of which it is composed may each one individually be brought into relation with the disturbing force.

Full directions for the preparation of sensitive Photographic paper are given in the second division of this work. The following is the theory of the process:—A sheet of paper is treated with solution of Chloride of Sodium or Ammonium, and subsequently with Nitrate of Silver; hence results a formation of Chloride of Silver in a fine state of division, with an excess of Nitrate of Silver, since the Silver bath is applied *after* the salting solution, and is made purposely of a greater strength.

Illustrative Experiment No. I.—Place a square of sensitive paper (prepared according to the directions given in the Second Part of the work) in the direct rays of the sun, and observe the gradual process of darkening which takes place; the surface passes through a variety of changes in colour until it becomes of a deep chocolate-brown. If the Light is tolerably intense, the brown shades are probably reached in from three to five minutes; but the sensibility of the paper, and also the nature of the tints, will vary much with the character of the organic matter present.

Experiment No. II.—Lay a device cut from black paper upon a sheet of sensitive paper, and compress the two together by means of a sheet of glass. After a proper length of exposure the figure will be exactly copied with the tint reversed: the black paper protecting the sensitive Chloride beneath, produces a *white* figure upon a dark ground.

Experiment No. III.—Repeat the last experiment, substituting a piece of lace or gauze-wire for the paper device. This is intended to show the minuteness with which objects can be copied, since the smallest filament will be distinctly represented.

Experiment No. IV.—Take an engraving in which the contrast of light and shade is tolerably well marked, and having laid it closely in contact with the sensitive paper, expose as before. This experiment shows that the surface darkens in degrees proportionate to the intensity of the light, so that the *half* shadows of the engraving are accurately maintained, and a pleasing gradation of tone produced.

In the darkening of Photographic papers, the action of the light is quite superficial, and although the black colour may be intense, yet the amount of reduced Silver which forms it is so small that it cannot be conveniently estimated by chemical reagents. This is well shown by the results of an analysis performed by the Author, in which the total weight of Silver obtained from a blackened sheet measuring nearly 24 by 18 inches amounted to less than *half a grain*. It becomes therefore of great importance in preparing sensitive paper to attend to the condition of the surface layer of particles, the action rarely extending to those beneath. The use of Albumen, Gelatine, etc., which will be explained in the eighth Chapter, has reference to this amongst other advantages, and secures a better and more sharply defined print.

THE NATURE OF THE CHEMICAL CHANGES PRODUCED BY LIGHT UPON COMPOUNDS OF SILVER.

Action of Light upon Chloride of Silver.—This may be studied by suspending pure Chloride of Silver in distilled water, and exposing it to the sun's rays for several days. When the process of darkening has proceeded to some extent, the supernatant liquid will be found to contain *free Chlorine*, or, in place of it, *Hydrochloric Acid* (HCl) and an Oxide of Chlorine (ClO), both of which are products of a subsequent action of the evolved Chlorine upon the water.

The luminous rays appear to loosen the affinity of the elements Chlorine and Silver for each other; hence a portion of Chlorine is separated, and the white Protochloride is converted into a violet *Sub*chloride of Silver. If an atom of Nitrate of Silver be present, the liberated Chlorine unites with it, displacing Nitric Acid, and forming again Chloride of Silver which is decomposed in its turn. The excess of Nitrate of Silver thus augments the darkening of Chloride of Silver, by rendering the chain of chemical affinities more complete, and preventing an accumulation of Chlorine in the liquid.

The violet-coloured compound, the product of the darkening action of light, has been spoken of by some writers as a mixture of Chloride of Silver and Metallic Silver, but the fact that white Chloride of Silver will darken in the sun's rays, even when covered with strong Nitric Acid, appears to indicate that a Subchloride of Silver is formed.

The properties of this Subchloride are as follows:—It is very little affected by Nitric Acid, but quickly acted on by those bodies which Photographers employ as fixing agents, viz. Ammonia, Hyposulphite of Soda, and Cyanide of Potassium; the greater part being dissolved by the fixing agent, and a minute portion of Metallic Silver remaining insoluble.

Chemical Changes on Organic Salts of Silver.—White Albuminate of Silver is soluble in Ammonia, and also in Hyposulphite of Soda; but after having been reddened by exposure to light, very little effect is produced upon it by these fixing agents. Gelatine saturated with Nitrate of Silver and exposed to light, loses its characteristic property of dissolving in hot water, but when treated with boiling solution of Potash, it is taken up, forming a clear liquid of a blood-red colour.

From these facts and others not mentioned, we infer that in the action of light upon Organic Salts of Silver, the Oxide of Silver loses oxygen and sinks to the state of a Suboxide just as Chloride of Silver parts with a portion of chlorine when exposed to light and becomes a Subchloride. The organic body absorbs the liberated oxygen, and the products are left in combination with each other. The present state of our knowledge will not allow of more than a general indication of the nature of these changes; no exact formulæ can be given.

Nature of the Blackening of Photographic Papers.—In this case both Chloride of Silver and Nitrate of Silver are present, supported by an organic basis. To ascertain the nature of the darkening action of light upon a surface of this kind, it is better to spread the Chloride upon a glass plate, and to make two experiments, adding organic matter in one, and omitting it in the other. Chloride of Silver does not readily adhere to glass unless the surface of the glass be finely ground, and even then very careful manipulation is required. A more simple plan is to employ *Collodion* as a vehicle for the Chloride, and this we may do with impunity, since it is known that Pyroxyline, the basis of Collodion, has comparatively little effect upon the Salts of Silver, and behaves towards them almost in the manner of an inert substance, such as glass or porcelain. Having therefore taken a sample of ordinary Collodion, dissolve in each ounce seven grains of Chloride of Zinc; then coat two glass plates in the usual way, allow them to become quite dry, and immerse in a Nitrate bath. Rear one of the plates on end to drain, but wash the other with water, and pour over it a little diluted Albumen, afterwards drying a second time, and redipping in the bath. In the course of a few hours, expose both to sunlight. It will be found that the Chloride of Silver upon Collodion alone, darkens to a violet-blue tint; but that on Albumen and Collodion mixed, changes to a deep olive-brown. Now apply a drop of Nitric Acid to the two plates; the violet subchloride will be very little affected, but the brown image containing a suboxide will dissolve. Next treat the plates with Ammonia; this will dissolve the violet and produce no effect upon the brown image. It is clear therefore, from the action of these tests, that the presence of Albumen makes an important difference in the nature and properties of the image.

But in order to investigate the subject thoroughly, the darkened plates must be examined *after*, as well as before treatment with a fixing agent, since a photographic picture cannot be said to be completed until it has passed through the bath of Hyposulphite of Soda. We therefore prepare a fresh series of films of Chloride and Nitrate of Silver in the manner above described, viz. some on dry Collodion, and others upon Albumen, and having, by repeated treatment with fresh Nitrate of Silver, and a long exposure to the sun's rays, obtained the maximum of darkening, we immerse them in solution of Hyposulphite of Soda, wash carefully, and dry. Comparing the two sets of images after fixing, we find those on the Collodion, grey by reflected light, and pale slaty-blue by transmitted light. The images on the Albumen, on the other hand, are of a dark olive-brown by reflection, and almost absolutely opaque when examined by transmission. The following tests are then applied :—*a. Mercury :* amalgamation with the Collodion image, but none with the Albumen. *b. Cyanide of Potassium :* no action on the grey and transparent image, but gradual solution of the brown opaque image. *c. Sulphuretted Hydrogen water :* darkens the image on Collodion, but gradually bleaches that on Albumen. *d. Permanganate of Potash*, if in dilute solution, scarcely acts on the slaty-blue image, but oxidizes the brown image.

Putting these facts together, we say, that photographs formed on pure Chloride and Nitrate of Silver consist of a Subchloride of Silver before fixing with Hyposulphite of Soda, and of Metallic Silver after fixing. In practice, however, it is found impossible to produce a picture on pure Chloride of Silver, the image being altogether too faint, and lacking depth of colour by reflected light. When Albumen, Gelatine, or analogous substances are present the image contains Suboxide of Silver combined with organic matter: and this combination is not entirely destroyed in the process of fixing, for although both Subchloride and Suboxide of Silver are instantly decomposed by fixing agents, yet the latter does not appear to be so when united with Albumen.

The action of tests upon the organic image will vary with the length of time the plates have been exposed to light. The more intense the blackening, the less evident is the action of solvents, such as the Cyanide of Potassium, etc. Hence the half-tones of a Photographic picture often dissolve in fixing, whilst the full shadows remain. Unstable Salts of Gold, on the other hand, when applied to an image on paper, deposit the metal more readily on those parts which have been completely blackened, and less so upon the lighter shades. Again, if Photographic papers be prepared with two different kinds of organic matter, as, for example, with Iceland moss in one case and Albumen in another, the images obtained will not exactly correspond in properties. And if, in a third experiment, the paper be rendered sensitive upon a solution of *Oxide* of Silver in place of Nitrate of Silver, the re-action with tests will again be different. Therefore, although the Photograph contains both organic matter and Silver, no certain formula can be given for its composition.

The consideration of the effects of organic matter in modifying the properties of the image will be resumed in the Chapter treating of photographic printing.

CHAPTER III.

ON THE DEVELOPMENT OF AN INVISIBLE IMAGE BY MEANS OF A REDUCING AGENT.

It has been shown in the previous Chapter that the majority of the Salts of Silver, both organic and inorganic, are darkened in colour on exposure to light, and, by the loss of Oxygen, Chlorine, etc., become reduced to the condition of *Sub*salts.

Many of the same compounds are also susceptible of a change under the influence of light, which is even more remarkable. This change takes place after a comparatively short exposure, and does not affect the appearance of the sensitive layer. The impression, however, although invisible at first, is brought out by treating the plate with certain chemical agents which are without effect on the original unchanged salt.

Experiments illustrating the Formation of an Invisible Image.—Take a sheet of sensitive paper, prepared with Iodide of Silver by the method given in the third Chapter of Part II., and having divided it into two parts, expose one of them to the luminous rays for a few seconds. No visible decomposition takes place, but on removing the pieces to a room dimly illuminated, and brushing with a solution of *Gallic Acid,* a manifest difference will be observed; the one being unaffected, whilst the other darkens gradually until it becomes black.

Experiment II.—A prepared sheet is shielded in certain parts by an opaque substance, and then after the requisite exposure, which is easily ascertained by a few trials, treated with the Gallic Acid as before; in this case the protected part remains white, whilst the other darkens to a greater or less extent. In the same way, copies of leaves, engravings, etc., may be made, very correct in the shading and much resembling those produced by the prolonged action of light alone upon the Chloride of Silver.

A great economy of time is effected by employing a substance like Gallic Acid to *develope* or bring out to view an invisible image, in preference to forming the picture by the direct action of light, unassisted by a developer. This is well shown in the results of some experiments conducted by M. Claudet in the Daguerreotype process: he found that with a sensitive layer of Bromo-Iodide of Silver, an intensity of light three thousand times greater was required if the use of a developer was omitted, and the exposure continued until the picture became visible upon the plate.

To increase the sensitiveness of Photographic preparations is a point of great consequence; and indeed, when the Camera is used, from the low intensity of the luminous image formed in that instrument, no other plan than the one above described would be practicable. Hence the advancement, and indeed the very origin, of the Photographic Art, may be dated from the first discovery of a process for bringing out to view an invisible image by means of a reducing agent.

The present Chapter is divided into two Sections:—first, the properties of the substances usually employed in reducing the Salts of Silver, with their mode of action; and second, the formation and development of the invisible image.

SECTION I.

The various Substances employed as Reducing Agents.

The most important of the developers are as follows:—Gallic Acid, Pyrogallic Acid, and the Protosalts of Iron.

GALLIC AND PYROGALLIC ACIDS.

a. *Gallic Acid.*—Gallic Acid is obtained from *Gall*

Nuts, which are peculiar excrescences formed upon the branches and shoots of the *Quercus infectoria* by the puncture of a species of insect. The best kind is imported from Turkey, and sold in commerce as Aleppo Galls. Gall Nuts do not contain Gallic Acid ready formed, but an analogous chemical principle termed *Tannic Acid*, well known for its astringent properties and employment in the process of tanning raw hides.

Gallic Acid is produced by the *decomposition and oxidation* of Tannic Acid when powdered galls are exposed for a long time in a moist state to the action of the air. By boiling the mass with water and filtering whilst hot, the acid is extracted, and, being sparingly soluble in cold water, crystallizes on cooling.

Gallic Acid occurs in the form of long silky needles, soluble in 100 parts of cold and 3 of boiling water; they are also readily soluble in Alcohol, but sparingly in Ether. The aqueous solution becomes mouldy on keeping, to obviate which the addition of a lump of Camphor or a drop or two of Oil of Cloves is recommended.

Gallic Acid is a feeble acid, scarcely reddening litmus; it forms salts with the alkaline and earthy bases, such as Potash, Lime, etc., but not with the oxides of the noble metals. When added to Oxide of Silver the metallic element is separated and the Oxygen absorbed.

b. *Pyrogallic Acid.*—The term *pyro* prefixed to Gallic Acid implies that the new substance is obtained by the *action of heat* upon that body. At a temperature of about 410° Fahr., Gallic Acid is decomposed, and a white sublimate forms, which condenses in lamellar crystals; this is Pyrogallic Acid.

Pyrogallic Acid is very soluble in cold water, and in Alcohol and Ether; the solution decomposes and becomes brown by exposure to the air. It gives an indigo-blue colour with Protosulphate of Iron, which changes to dark green if any Persulphate be present.

Although termed an *acid*, this substance is strictly *neutral:* it does not redden litmus-paper, and forms no salts.

It has an affinity for Oxygen, which is greatly augmented by the presence of an alkali: a mixture of this kind made by adding Liquor Potassæ to Pyrogallic Acid, may conveniently be employed for absorbing the Oxygen contained in atmospheric air.

Commercial Pyrogallic Acid is often contaminated with empyreumatic oil, and also with a black insoluble substance known as *Metagallic Acid*, formed when the heat is raised above the proper temperature in the process of manufacture.

THE SALTS OF IRON.

The combinations of Iron with Oxygen are somewhat numerous. There are two distinct Oxides which form Salts, viz. the Protoxide of Iron, containing an atom of Oxygen to one of metal; and the Peroxide, with an atom and a half of Oxygen to one of metal. As *half atoms*, however, are not allowed in chemical language, it is usual to say that the Peroxide of Iron contains three equivalents of Oxygen to two of metallic Iron.

Expressed in symbols, the composition is as follows:—

Protoxide of Iron, FeO.
Peroxide of Iron, Fe_2O_3

The Proto- and Persalts of Iron do not resemble each other in their physical and chemical properties. The former are usually of an apple-green colour, and the aqueous solutions almost colourless, if not highly concentrated. The latter, on the other hand, are dark, and give a yellow or even blood-red solution.

The following experiment will serve to illustrate the properties of both classes of salts:—Take a crystal of Protosulphate of Iron, and, having reduced it to powder, pour a little Nitric Acid upon it in a test-tube. On the application of heat, abundance of fumes will be given off, and a red solution obtained. The Nitric Acid in this reaction imparts Oxygen, and converts the *Proto*sulphate entirely into a *Per*sulphate of Iron. It is this feature, viz. the tendency to absorb Oxygen, and to pass into the state of

Persalts, which makes the Protosalts of Iron useful in Photography.

There are two Protosalts of Iron commonly employed by Photographers: the Protosulphate and the Protonitrate of Iron.

a. *Protosulphate of Iron.*—This salt, often termed *Copperas* or *Green Vitriol*, is an abundant substance, and used for a variety of purposes in the arts. Commercial Sulphate of Iron, however, being prepared on a large scale, requires recrystallization to render it sufficiently pure for Photographic purposes.

Pure Sulphate of Iron occurs in the form of large transparent, prismatic crystals, of a delicate green colour: by exposure to the air they gradually absorb Oxygen and become rusty on the surface. Solution of Sulphate of Iron, colourless at first, afterwards changes to a red tint, and deposits a brown powder; this powder is a *basic* Persulphate of Iron, that is, a Persulphate containing an excess of the oxide or *base*. By the addition of Sulphuric or Acetic Acid to the solution, the formation of a deposit is prevented, the brown powder being soluble in acid liquids.

The Crystals of Sulphate of Iron include a large quantity of water of crystallization, a part of which they lose by exposure to dry air. By a higher temperature, the salt may be rendered perfectly *anhydrous*, in which state it forms a white powder.

b. *Protonitrate of Iron.*—This salt is prepared by double decomposition between Nitrate of Baryta or Lead and Protosulphate of Iron. It is an unstable substance, and crystallizes with great difficulty; its aqueous solution is pale green at first, but very prone to decomposition, even more so than the corresponding Sulphate of Iron.

THE REDUCTION OF SALTS OF SILVER BY DEVELOPING AGENTS.

Development is essentially a process of *reduction*, or, in other words, of *deoxidation*. If we take a certain metal, we may, by means of Nitric Acid, impart Oxygen to it, so that it becomes first an Oxide, and afterwards, by solution of the Oxide in the excess of acid, *a salt*. When this salt is formed, by a series of chemical operations the reverse of the former it may be deprived of all its Oxygen, and the metallic element again isolated.

The degree of facility with which oxidation as well as reduction is performed, depends upon the affinity for Oxygen which the particular metal under treatment possesses. In this respect there is considerable difference, as may be shown by a reference to the two well-known metals, Iron and Gold. The first becomes speedily tarnished and covered with rust, whilst the other remains bright even in the fire. It is indeed possible, by a careful process, to form Oxide of Gold; but it retains its Oxygen so loosely that the mere application of heat is sufficient to drive it off, and leave the metal in a pure state.

Silver, Gold, and Platinum all belong to the class of *noble* metals, having the least affinity for Oxygen. Their Oxides are therefore unstable, and any body tending strongly to absorb Oxygen will reduce them to the metallic state.

Observe, therefore, that the substances employed by the Photographer to assist the action of light, and to develope the picture, act by removing Oxygen. The Sensitive surface is thus *reduced*, more or less completely, in the parts touched by light, and an opaque deposit results which forms the image.*

Reduction of Oxide of Silver.—To illustrate this conveniently, the Oxide of Silver should be in a state of solution; water dissolves Oxide of Silver very sparingly, but it is freely soluble in Ammonia, forming the liquid known as Ammonio-Nitrate of Silver. If, therefore, a little of the Ammonio-Nitrate of Silver be placed in a test-tube, and solution of Sulphate of Iron be added to it, immediately it becomes discoloured, and a deposit settles to the bottom.

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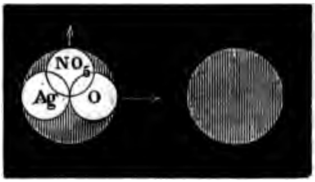
* These remarks do not apply to the vapour of Mercury employed as a developing agent in the Daguerreotype. The chemistry of that process will be explained in a separate Chapter.

This deposit is metallic Silver, produced by the reducing agent appropriating to itself the Oxygen previously combined with the metal. As metallic Silver does not dissolve in Ammonia, the liquid becomes turbid, and the metal subsides in the form of a bulky precipitate.

Reduction of the Salts of Silver.—Salts of Silver soluble in water, are reduced by developing agents in the same manner as Oxide of Silver, but more slowly. The presence of an acid united with the base is a hindrance to the process, and tends to keep the oxide in solution, especially when that acid is powerful in its affinities. To illustrate the effect of the acid constituent of the salt in retarding reduction, take two test-tubes, the one containing Ammonio-Nitrate, and the other ordinary Nitrate of Silver—a single drop of solution of Sulphate of Iron added to each will indicate an evident difference in the rapidity of decomposition.

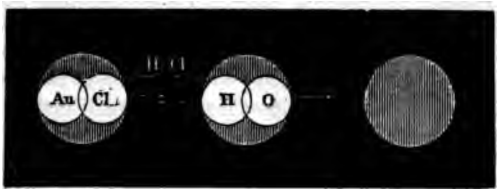
The following simple diagram may assist the comprehension of the change:—



Compound Atom of Nitrate of Silver. Atom of Sulphate of Iron.

The symbol Ag represents Silver, NO_5 Nitric Acid, and O, Oxygen. Observe that the molecules Ag and O separate, the latter passing to the reducing agent; the NO_5 is also liberated, and may either remain in the liquid in a free state, or be de-oxidized by the developer.

There are some metallic salts, such for instance as the Chlorides and Iodides, which do not contain Oxygen; but these admit of reduction by developing agents, if *water* be present. To illustrate this, take a solution of Chloride of Gold, and add to it a little Sulphate of Iron. A yellow deposit of metallic Gold soon forms, and the supernatant liquid is found, by testing, to be acid from free Hydrochloric Acid. The following simple diagram, in which however the *number* of the atoms concerned is omitted may explain this reaction.



Compound Atom of Chloride of Gold. Compound Atom of Water. Atom of Sulphate of Iron.

In the above diagram the symbol Au represents Gold, Cl Chlorine, H Hydrogen, and O Oxygen. An atom of water is decomposed, the Hydrogen combining with the Chlorine to form Hydrochloric Acid (HCl), and the Oxygen passing to the reducing agent as before.

Hence there would be no theoretical difficulty in supposing a reduction of *Iodide* of Silver, if we associated with it an atom of water to furnish the Oxygen. We shall presently see however that pure Iodide of Silver is unaffected by a reducing agent, and that the compound which blackens on the application of the Pyrogallic Acid is an Iodide with excess of Nitrate of Silver (p. 40).

Presence of Free Acids, etc., in Development.—Acids exercise a retarding effect upon the reduction of salts of Silver by the developing agents, and especially those acids which, like Nitric Acid, possess oxidizing and solvent properties upon metals. Solution of Pyrogallic Acid mixed with Nitrate of Silver produces a deposit immediately; but if a little Acetic Acid be previously added, the precipitation is more gradual, and when both solutions are strongly acidified with Nitric Acid, it is for a time suspended. On the other hand, *alkaline* liquids, as before shown, produce an opposite effect, and favour quick reduction.

Comparative Strength of reducing Agents.—Sulphate of Iron acts with rapidity. Nitrate of Iron and Gallic Acid are both feeble reducing agents. Pyrogallic Acid is stronger, a smaller quantity sufficing to produce the effect. Oil of Cloves, Grape Sugar, Aldehyde, Honey, etc., are capable of reducing Salts of Silver, but they act too slowly to be employed with advantage in Photography.

Effect of Temperature.—Reduction of the Oxides of noble metals proceeds more rapidly in proportion as the temperature rises. In cold weather it will be found that the development is slower than usual, and that greater strength of the reducing agent and more free Nitrate of Silver is required to produce the effect. The action of Sulphate of Iron, however, is considered to be less affected by depression of temperature than that of Pyrogallic Acid.

On the other hand, if the heat of the atmosphere be excessive, the tendency to rapid reduction will be greatly increased, the solutions decomposing each other almost immediately on mixing. In this case the remedy will be to use Acetic Acid *freely*, or in place of it Citric Acid, which, as a retarding agent, is at least twenty times stronger than Acetic Acid.

Varieties of Colour in deposited Silver.—The precipitate of metallic Silver obtained by the action of reducing agents upon the Nitrate, varies much in colour and in general appearance. If Gallic or Pyrogallic Acid be employed, it is a black powder; whilst the Salts of Iron, and especially the same with free Nitric Acid added, produce a sparkling precipitate, resembling what is termed *frosted silver*. Grape Sugar and many of the essential oils, such as Oil of Cloves, etc., separate the metal from Ammonio-Nitrate of Silver in the form of a brilliant mirror film, and are often employed in silvering glass.

In remarking upon these peculiarities in the molecular condition of precipitated Silver, it should be observed that the appearance of a metal whilst in mass is no indication of its colour when in the state of fine powder. Platinum and Iron, both bright metals, and susceptible of a high polish, are dull and intensely black when in a fine state of division; Gold is of a purple or yellowish brown; Mercury a dirty grey.

SECTION II.

The Formation and Development of the Latent Image.

It was shown in the second Chapter that the continued action of white light upon certain of the Salts of Silver resulted in the separation of elements like Chlorine and Oxygen and the partial *reduction* of the compound. We have seen in this Chapter that bodies possessing affinity for Oxygen, such as Sulphate of Iron and Pyrogallic Acid, produce a similar effect; acting in some cases with great energy and precipitating metallic Silver in a pure state.

In forming an extemporaneous theory on the production of the Photographic image by development, it would therefore be natural to suppose that the process consisted in commencing a reducing action upon the sensitive surface by means of the luminous image of the Camera, and afterwards completing or carrying on the same by the application of the developing solution. We may remark however that this hypothesis is not the one most strongly supported by facts, and that it will certainly lead us astray if too far pressed. The idea of the luminous image in the Camera originating a chemical change, and the reducing agent carrying on that change to its completion, might lead to the inference that the two agencies were exactly similar in their mode of operation, and that the one could be substituted for the other: that when for instance the exposure in the Camera had been very brief the defect would be remedied by prolonging the development. Such a notion is quite erroneous. A definite time is occupied in the formation of the invisible image, which cannot be shortened or extended beyond its proper limits with impunity. So far from the action of the developing solution being facilitated when the plate has been left in the Camera for an unusually long time, it is often retarded thereby; and on the other hand, unless the exposure be sufficient, it will be in vain to expect to produce a picture by strengthening the reducing agent or keeping it upon the plate for a longer time. Thus we see that "the invisible image" has a real existence, and that its formation by the solar ray is a phenomenon quite distinct from any after-process of development.

HYPOTHESIS ON THE NATURE OF THE INVISIBLE IMAGE.

When a sensitive film containing a Salt of Silver is exposed in the Camera, and receives a latent impression capable of subsequent development, an inquiry arises as to the exact condition of the film-particles on which the light has acted. The most careful inspection, even with the aid of a microscope, fails to detect any difference between the exposed and non-exposed portions of the plate. Chemical solvents likewise act in the same manner both before and after the insolation, thus showing that there is no actual separation of the elements of the film, analogous to the elimination of Chlorine from Chloride of Silver by the prolonged action of the sun's rays.

The formation of the invisible image is universally allowed to be a molecular and not a chemical change. The following diagrams will assist mechanically in conveying an idea of what we mean by a molecular change.

Fig. 1.

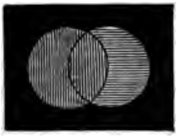
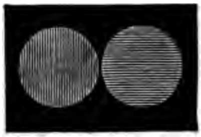


Fig. 2.



Let fig. 1 represent the Iodide of Silver in its norma state, and fig. 2 the same Iodide after its impression in the Camera. The chemical composition has not been changed, for supposing one of the circles to represent Iodine and the other Silver, we have in both figures a single atom of each. The arrangement of the constituent atoms however has been modified in the second figure, where they are so placed as to touch each other only at the edges. Let it be borne in mind that this representation is purely hypothetical. We observe certain differences in the properties of the Iodide after its insolation, and suppose them to indicate corresponding differences in molecular arrangement; but we cannot speak with certainty, since the ultimate atoms of bodies are too minute to come within the range of our observation.

We now proceed to examine further the tangible differences between the impressed and the non-impressed atom of Iodide of Silver. If the two be exposed for a short time over Mercury slightly warmed, the metallic vapour will condense upon the former, but not upon the latter; and in this way the latent picture is made visible in the Daguerreotype process. So again if Nitrate of Silver previously mixed with a reducing agent be applied to the same two atoms, it will be seen that the impressed or modified Iodide hastens the decomposition of the mixture, whereas the Iodide prepared in total darkness exercises no such effect. We have indeed learnt from the observations in the last Section that reducing agents themselves decompose Nitrate of Silver, and throw down the metal in a pure form. This reduction however is usually slow and gradual, and when a little free acid, such as Nitric or Acetic Acid, is added, the mixture remains perfectly clear for a period of five minutes or longer. Prepare therefore such a mixture with the proportions correctly adjusted, and drop into it two particles, one of the ordinary and the other of the impressed Iodide of Silver; when it will be found that the first remains yellow, but that the second immediately becomes black and is incrusted with Metallic Silver.

There are other and more familiar instances of the surfaces of bodies undergoing a molecular change, not to be detected by the eye, but yet altering their mechanical properties. If for example we place lumps of Camphor in a large bottle or globe of glass opposite to a window, we find that a portion of the Camphor evaporates and condenses in the form of glittering crystals on the side of the bottle exposed to the light. The action of the light appears to modify the surface of the glass in some unexplained manner, so that it offers an attraction to the crystals. The molecular disturbance however, whatever be its nature, is merely temporary, since if the position of the bottle be changed, the crystals will evaporate from the side darkened, and pass across to that which faces the light.

Another experiment, equally instructive, may be conducted as follows:—Take a clean glass vessel, and having poured into it a strong aqueous solution of Chloride of Potassium, add a little Tartaric Acid, and stir briskly with a glass rod. In a few moments the parts of the glass touched by the rod will be marked by a line of minute crystals. In this case there is a disposition in the liquid to crystallize; but the *scratched state of the glass*, where the rod has touched it, facilitates the change, and determines the point at which the crystallization shall commence. The deposit is adherent and is not removed by emptying the capsule of its contents and washing it out with alcohol: warm water, however, dissolves the crystals of Bitartrate, and the surface of the glass is then found intact; the scratched condition, as we have termed it, being temporary and quite invisible.

One additional illustration of molecular in contradistinction to chemical change will suffice. When an engraving which has been framed and suspended for a length of time is taken down to be cleaned, it will sometimes happen that the glass, however carefully polished by rubbing, will exhibit the outlines of the picture when breathed on. The breath settles in certain parts and not in others, in consequence of variations in the surface condition. When the glass is put aside, the invisible image gradually vanishes, and the molecules return to their original state.

Granting, therefore, that a ray of white light in acting on Iodide of Silver, so modifies it that it acquires the property of accelerating chemical change in the mixture known to Photographers as the developing agent, we observe in the next place, that it is not necessary to suppose that the invisible modification is permanent, or that the particles of the Iodide, once disturbed, cannot afterwards be restored to their normal state. On the contrary, there are facts which prove that the invisible image may completely disappear, leaving the plate in a condition to receive a second impression in the camera.

Mechanical diagrams may here be again employed; and their use will be free from objection, if it be understood that they are meant only to assist in fixing facts upon the mind of the reader, and like a system of artificial memory, may be laid aside when this important object has been accomplished.

Fig. 1.

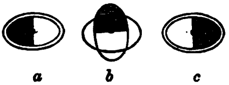


Fig. 2.

In the first figure we see two ovals, slightly different in size, and turning on a common centre; in (*a*) their long diameters correspond, but in (*b*) they cross each other, whilst in (*c*) they are made to coincide once more by a further action of the same force. In fig. 2 we have the more familiar illustration of waves: first an elevation, then a corresponding depression. Now in the photographic process we find that the invisible effect of the light rises gradually to a certain pitch of intensity, but beyond that it appears to descend as it were on the other side: hence the particle of Iodide of Silver first acquires the property of blackening the developer, but loses it again if left too long in the Camera.

THE DEVELOPMENT OF THE INVISIBLE IMAGE.

The amateur commencing the study of Photography will probably form an incorrect idea of the real nature of a developing agent. Being in the habit of applying to the surface of the wet Collodion a solution of Pyrogallic Acid or of Sulphate of Iron, he terms these compounds "the developers," and forgets that a floating layer of solution of Nitrate of Silver is also present, derived from the bath. To impress upon the mind the fact that the developer is not the simple reducing agent, but the same *mixed with Nitrate of Silver*, let the following experiment be made. Coat a plate with Iodized Collodion, pass it through the Nitrate Bath, and wash it carefully back and front with distilled water. Now expose for an instant to diffused daylight, and apply the Pyrogallic Acid: the plate will remain perfectly clear and transparent. The invisible impression however is truly present, and the insolated Iodide is ready to play its part, but no blackening takes place, because the reducing agent has nothing to act upon. Let the Pyrogallic Acid therefore be poured back into a measure containing a few drops of solution of Nitrate of Silver and applied a second time to the plate, when the film will begin to darken and continue to do so until it is quite opaque.

The second stage of the development.—This consists in strengthening the image first formed, by an additional deposit of Silver. Take a sensitive Collodion plate, and having impressed an invisible image upon it by a proper exposure in the Camera, remove it to the dark room, and pour over it solution of Pyrogallic Acid. When the picture has fully appeared, stop the action by washing the plate with water. An examination of the image at this stage will show that it is perfect in the details, but pale and translucent. Now take the plate and treat it with Pyrogallic Acid to which fresh Nitrate of Silver has been added; immediately the picture will become much blacker, and will continue to darken, even to complete opacity, if the supply of Nitrate be kept up. The same result may be obtained after the Iodide of Silver has been removed from the plate by Hyposulphite of Soda or Cyanide of Potassium; and in such a case it is evident that the additional deposit upon the image must be produced from the Nitrate of Silver and not from the Iodide of Silver. Observe also, that this additional deposit *forms only upon the image*, exhibiting no affinity for the unaltered Iodide upon the part of the plate corresponding to the shadows of the picture, but attaching itself in preference to those parts already blackened by the developer.

The second stage of the development, in which a feeble image is strengthened and rendered more opaque, is a process bearing a close resemblance to the growth of a crystal in a saturated liquid, by aggregation of fresh particles; and after the picture has reached its full density, a series of elevations may often be seen upon the plate, corresponding to the lines of the image.

OBJECTIONS TO THE FOREGOING VIEWS CONSIDERED.

The theory of the formation and development of the atent image given in the preceding pages was not originated by the author of this work, nor can he at present specify any one individual to whom it may be ascribed. Objections have been urged against it, and other hypotheses adopted in preference, not only in this country but also in France. It has been said for instance that the process of photographic printing upon Chloride of Silver nvolves a partial reduction of the Chloride by the action of light, and hence it is reasonable to suppose that the Iodide of Silver suffers reduction in the developing process. We must bear in mind however that there is a great difference in the intensity of the light to which the sensitive surface is subjected in the two cases mentioned, and not only so, but that the Iodide of Silver is more difficult to reduce than the Chloride. In fact, as we have already shown, the solar ray has no effect in discolouring pure Iodide of Silver, although it quickly blackens pure Chloride of Silver. If the invisible image were simply a disturbance of ultimate particles, rendering their after-separation by the reducing agent more easy, we should expect to find Chloride of Silver receiving the image of the

Camera with greater rapidity than Iodide of Silver. The contrary however is the case, and we are probably within the mark in stating the sensitiveness of Iodide of Silver to be ten times greater than that of Bromide and sixty times greater than that of Chloride of Silver.

Another argument militating strongly against the view often expressed that the latent image consists of Iodide of Silver reduced in inappreciable quantities, or of Iodide of Silver with an increased tendency to reduction, is the fact before mentioned, that the rapidity of the development is not in proportion to the length of the exposure in the Camera. On the over-exposed sky of a landscape the Iodide will sometimes remain yellow and unchanged throughout the whole process, whilst the less exposed parts of the plate darken under the influence of the developer.

The opponents of the views which we have given of the purely molecular character of the disturbance in the Camera base their objections chiefly on phenomena observed in the practice of the dry Collodion processes. It is not unusual in such methods to obtain visible indications of the picture upon the surface of the film before the developer is applied; and even where no such indications present themselves, there yet often exists a remarkable difference between the exposed and the non-exposed parts to which as yet we have not directed the reader's attention. Mr. Young, of Manchester, was the first to notice the phenomenon, and to show that if an exposed plate be immersed in solution of Hyposulphite of Soda until the yellow Iodide of Silver is dissolved, a picture will still appear on applying the usual developing mixture. The effect cannot be obtained on a wet Collodion plate and only imperfectly on a plate preserved by honey, the best substance to exhibit it being Albumen. The Author has experimented with a view of accounting for a phenomenon so remarkable as the development of an invisible image upon a plate previously cleared of its Iodide of Silver, and the explanation which he would suggest is as follows :—Pure Iodide of Silver is molecularly modified by the Camera image, but its properties as regards the action of Hyposulphite of Soda are unaffected thereby: upon a plate so constituted no image could be developed after fixing. The sensitive surface of the Collodion photographer is never however an absolutely pure Iodide of Silver, and sometimes very far from being so. It contains traces of an organic compound of Silver in the wet Collodion process, and more appreciable quantities of the same in the dry processes. Now, with a compound film of this kind, it may be supposed that whilst the Iodide of Silver undergoes its peculiar change in the Camera, the organic combination of Silver likewise changes, but in a different manner. Without altering in appearance it gradually loses its solubility in fixing agents, so that when the Hyposulphite of Soda is applied its removal is not effected. We do not however perceive any picture upon the film, because the organic combinations of Silver are transparent in thin layers, even when they contain Iodide of Silver. An Albumino-Iodide of Silver for instance may be prepared in clear and colourless lumps like the finest jelly, and it is not difficult to conceive that such a substance may remain in an invisible condition upon Mr. Young's plates even after fixing.

If the above Hypothesis be correct, there exist two varieties of the invisible image: first, that upon simple Iodide of Silver which enables it to condense Mercury or to determine chemical change in the unstable developer; secondly, the image upon Iodide of Silver placed in contact with an organic compound of Silver. In the latter case the movement of the particles of the Iodide is supposed to be propagated to the other body, and changes are thus originated, visible or latent, according to the duration of the exposure, and the properties of the superadded substance. An organic Salt of Silver contains in itself the elements of its own reduction, and hence we are not surprised to find a catalytic action exerted upon it by the actinically excited Iodide of Silver.

CAUSES WHICH AFFECT THE SENSITIVENESS OF IODIDE OF SILVER.

By the term sensitiveness we understand a facility of receiving an impression from a very feeble ray of light, or of receiving it quickly from a bright ray. This impression however need not be followed by a vigorous or intense development, in order to constitute sensitiveness. On the contrary, it often happens that the most sensitive film yields a feeble picture, and when the Iodide is so prepared as to produce an opaque picture, then it is less sensitive, and requires to be exposed in the Camera for a longer time.

It has already been stated that although Iodide of Silver is less affected by direct sunlight than Bromide or Chloride of Silver, yet that it is more sensitive to the reception of the invisible image than either of those compounds. Placing Iodide of Silver therefore at the head of the list, we remark that, in the state in which it is used upon Collodion, it possesses the highest degree of sensitiveness when there is an excess of Nitrate of Silver; and if the experiment be made of washing the plate carefully with distilled water so as to remove the free Nitrate, a longer exposure in the Camera will be required. The sensitiveness does not, however, increase uniformly with the amount of free Nitrate, and it has been found in the Collodion process that no advantage can be gained by using a solution of Nitrate of Silver stronger than that usually recommended for the Bath.

Strong acids, and especially oxidizing acids like Nitric Acid, greatly diminish the sensitiveness of Iodide of Silver. Even a weak vegetable acid, such as the Acetic, has a similar though less decided effect, and if the Collodion film be rendered very acid with Acetic Acid before its exposure in the Camera, it will be found impossible to take a picture rapidly, even after strengthening the developer to the utmost limits.

It has long been remarked that the use of bodies like Albumen, Gelatine, Caseine, etc., which combine with Oxides of Silver, retards the action of light upon Iodide of Silver, and this is believed to be one principal reason why the Collodion film is so sensitive, viz. because Pyroxyline, the basis of Collodion, is a substance peculiarly indifferent to the Salts of Silver, and exhibits very little tendency to combine with them. The Photographer often employs Albumen, but he does so with a view of increasing the opacity of the image, and not for the purpose of adding to the sensitiveness. Whilst discussing Mr. Young's experiments we have distinguished between simple Iodide of Silver and Iodide with addition of organic compounds. The latter combination gives the more vigorous picture, but the former is superior in sensitiveness.

The great sensitiveness of Iodide of Silver on Collodion may also be due in a measure to mechanical causes. The loose state of coagulation in a Collodion film and the exquisitely fine state of division in which the particles are deposited must be favourable to molecular and chemical change. It will be seen as we proceed that success in this process depends very much upon correctly balancing the different solutions, in order that the Iodide of Silver may be thrown down in a state favourable to penetration by the developer.

Before passing to the next division of our subject, it may further be remarked, that in any Photographic process in which an invisible image is produced, the time occupied in forming that image will vary more or less with the nature of the agent by which it is to be developed. Bodies like the Protosulphate of Iron, possessing a strong affinity for Oxygen, will throw down Metallic Silver upon a surface of Iodide of Silver which has not undergone a sufficiently decided modification in the Camera to be affected by a weaker developer like Gallic Acid. It is probable that the future of instantaneous Photography, lies in the discovery of a developer even more unstable than a mixture of Sulphate of Iron and Nitrate of Silver; for the greater the instability, the less the need of a previously disturbing force to originate motion in the particles.

The controlling influence of the developer upon the sensitiveness of Iodide of Silver, must be borne in mind in instituting comparisons between the Daguerreotype and the Collodion process. The employment of ***Bromine*** in conjunction with Iodine increases the sensitiveness of the Daguerreotype, but we have no reason to suppose that such would be the case if the image were developed in a different manner. The vapour of Mercury condenses more readily upon the insolated *Bromo*-iodide than upon the simple Iodide of Silver, but another vapour might condense less readily, and experiment is the only safe guide.

Whilst upon this subject we also remark that the Iodide of Silver formed in the manner described in the tenth Chapter on the Daguerreotype, ought not to be compared photographically with Iodide of Silver thrown down from aqueous solutions. In the case of the metal plate there is a substratum of Metallic Silver, and it is not certain that the composition of this Iodide corresponds to that precipitated in the moist way. The action of light upon it certainly differs, for whereas the humid Iodide remains unaffected in the sun's rays, the Iodide of the Daguerreotypist gradually becomes insoluble in solution of Hyposulphite of Soda.

ILLUSTRATIONS OF ABNORMAL DEVELOPMENT.

The characteristics of the proper development of a latent image are—that the action of the reducing agent should cause a blackening in the parts touched by light, but produce no effect upon those which have remained in shadow. In operating both on Collodion and paper, however, we find a liability to failure in this respect; the film beginning, after the application of the developer, to change in colour to a greater or less extent over the whole surface.

Let us see how the above defect, known to the Photographer as "fogging," may be originated. Supposing the invisible image to be duly formed, it is yet necessary for its correct development that a proper balance should be maintained between the constituents of the developer. The reducing agent must not be too powerful, nor the quantity of Nitrate of Silver too large, otherwise although the deposited Silver will fall principally upon the image, a portion of it will be thrown down upon the shadows. It will also be found that the quantity of Nitrate of Silver being correctly balanced, fogging will certainly ensue if a little of this Nitrate be changed into *Oxide* of Silver by the addition of an alkali, since the tendency to reduction is then so strong that it cannot be controlled. Even when the Nitrate is accurately neutral, care and avoidance of all disturbing causes will be required to prevent a deposition of Silver upon the shadows of the image; especially when Nitrite of Silver or Acetate of Silver are present, both of which salts are more easily reduced than the Nitrate of Silver.

The use of *Acid* is the principal resource in obviating cloudiness of the image. Acids lessen the facility of reduction of the salts of Silver by developing agents (p. 33), and hence when they are present the metal is deposited more slowly, and only on the parts where the action of the light has so modified the particles of Iodide as to favour the decomposition: whereas if acids be absent, or present in insufficient quantity, the equilibrium of the mixture of Nitrate of Silver and reducing agent which constitutes the developer is so unstable, that any rough point or sharp edge becomes a centre from which the chemical action, once started, radiates to all parts of the plate.

Observe, however, that although we employ free acids in the developer to regulate the process and prevent the chemical actions from running riot, yet if we carry the proportion of the acid too far, or employ too strong an acid, we may originate the very defect we wish to avoid. Excess of Nitric Acid is a cause of fogging, if not as potent as excess of alkali, yet very decided. In this case the opposition to reduction is so strong, that for a long time after applying the developer to the plate no Silver is deposited:

eventually spangles of metal are seen, which adhere like sparkling dust to the shadows.

A more or less evident amount of fogging must be anticipated when the exposure in the Camera was too short. The latent image being in such a case very weak and imperfectly formed, does not act properly in attracting the Metallic Silver from the developer. When Nitrate of Silver and a reducing agent are present at the same time upon a film, Metallic Silver must very shortly fall upon some portion of the plate; hence the best security against fogging is a vigorous latent image, because in that case the action is so rapid upon the exposed parts that the energy of the developer is soon spent. Those films of Iodide of Silver which are prepared with especial reference to the production of vigorous images always give clean pictures, whereas the more sensitive Iodide of Silver is very liable to fog, since the latent image, although quickly formed, is not very deep or decided.

Spots upon the plate are instances of abnormal development, which may often be explained in a similar manner. In such a case the latent image upon the Iodide of Silver is not always sufficiently vigorous to exhaust with rapidity the mixture of reducing agent and Nitrate of Silver which constitutes the developer. Each spot exhibits, it is true, a central nucleus of extraneous matter, but this does not invalidate the argument. Such microscopic nuclei are always present upon the sensitive film to a greater or less extent, but if the invisible image be well formed, they are not so liable to increase in size during development. Full occupation must, so to speak, be provided for the developer, otherwise it will search out these minute particles, and surround them with deposited Silver. Filtering of solutions and avoidance of dust are useful remedies for spots, but so likewise is attention to the state of the sensitive film as regards vigorous and intense development. If however the energy of development be too great, the spots may recur; just as fogging of the film is sometimes due to deficiency of acid, and sometimes to excess of acid.

RESEARCHES OF M. MOSER AND OTHERS ON INVISIBLE IMAGES.

The papers of M. Ludwig Moser 'On the Formation and Development of Invisible Images,' published in 1842, explain so clearly many remarkable phenomena of occasional occurrence in the Photographic processes, that no apology need be offered for referring to them.

His first proposition may be stated thus:—"If a polished surface has been touched in particular parts by any body, it acquires the property of precipitating certain vapours on these spots differently to what it does on the other untouched parts." To illustrate this, take a thin plate of metal, having characters *excised;* warm it gently, and lay it upon the surface of a clean mirror glass for a few minutes: then remove, allow to cool, and *breathe* upon the glass, when the outlines of the device will be distinctly seen. A plate of polished Silver may be substituted for the glass, and in place of developing the image by the breath, it may be brought out by Mercurial vapour.

The second proposition of M. Moser was as follows:—"*Light* acts on bodies, and its influence may be tested by vapours that adhere to the substance."—A plate of mirror glass is exposed in the Camera to a bright and intense light; it is then removed and breathed upon, when an image before invisible will be developed, the breath settling most strongly upon the parts where the light has acted. A plate of polished Silver may be used as before instead of glass, the vapour of Mercury or of water being employed to develope the image. A Silver plate exposed to the vapour of Iodine until Iodide of Silver has formed upon its surface, is still more sensitive to the influence of light, and receives a very perfect impression under the subsequent action of the Mercury.

The above and other experiments of M. Moser have a practical significance, for it has since been found that the same condition of surface which causes a vapour to settle in a peculiar manner may also affect the behaviour of the Iodide of Silver when treated with a mixture of Nitrate of Silver and a reducing agent. Thus, if a clean glass plate be touched in certain spots by the warm finger, the impression soon disappears, but is again seen on breathing upon the glass; and if this same plate be coated with a very delicate layer of Iodized Collodion and passed through the Nitrate bath, the solution of Pyrogallic Acid will often produce a well-defined outline of the figure even before the plate has been exposed in the Camera. This experiment is an instructive one, and shows the necessity of cleaning the plates used in Photography with care. If there be any irregularity in the manner in which the breath settles upon the glass when it is breathed on, a condition of surface exists at that point which will probably so modify the layer of Iodide of Silver, that the action of the developing fluid will be in some way interfered with.

Glass plates with Collodion pictures on them should be cleaned very carefully before being again used, or the old impression will re-appear during development. Plates packed in sheets of newspaper often show the letters in the same way when the Pyrogallic Acid is applied: traces of organic matter in all probability are present in the superficial pores of the glass, and it is only by long soaking in chemical solutions that these invisible images can be destroyed. It may in every case be assumed that the existence of the invisible image can be detected by breathing, and that a glass which does not affect the breath is photographically clean.

M. Moser in the same series of papers calls attention to the peculiar phenomena resulting from over-action of light. "If light," he says, "acts on Iodide of Silver, it imparts to it the power of condensing mercurial vapours, but if it acts beyond a certain time, it then diminishes this power, and at length takes it away altogether." This observation, like the last, is a practical one, for in all photographic processes we have to contend against the phenomenon known as solarization. Over-exposure in the Camera will invariably weaken the action of the developer more or less, but nevertheless the tendency to solarize may be overcome in a measure by associating other substances with the Iodide of Silver, so as to impart greater stability to the invisible image. Bromide of Silver appears to exercise such an effect, as also does an acid condition of the film, in contradistinction to an alkaline condition. The presence of organic Salts of Silver in the film likewise influences the amount of solarization.

Observations by Norris and others.—When a sensitive Collodion plate is washed in water before its exposure in the Camera, a mixture of Pyrogallic Acid and Nitrate of Silver is required to develope it. The mixture is usually made before the developer is applied to the film, and this is of more importance than would appear. If the Pyrogallic Acid solution be used alone without any Nitrate of Silver, it will frequently *obliterate* the latent impression, so that a second picture may be taken upon the same plate. Such however is not invariably the case; if a mere trace of Nitrate of Silver remain in the pores of the Collodion, there will be development instead of obliteration. A washed Collodion film may have its free Nitrate of Silver restored to it by dipping in the Bath after exposure, but it will, as a rule, develope with unusual energy after such treatment, and the picture will be taken by a shorter exposure than if the plate were simply flooded with a mixture of Pyrogallic Acid and Nitrate of Silver.

Dilute acids gradually obliterate the latent image on washed Collodio-iodide of Silver. When an exposed plate is left for a time over the vapour of Acetic Acid, the impression gradually disappears and the film returns to a sensitive condition. On repeating this experiment, the author finds that the second latent image requires a longer exposure in the Camera, and developes in a somewhat different manner from the first.

Dry Iodide of Silver on Collodion, gradually loses its power of receiving the latent image, when placed in contact with certain other bodies. Thus the extreme edges of dry plates, where they touch the grooves of the carrying-box, often remain transparent on developing, and exhibit no indications of an impression. Traces of organic matter have a similar effect on the Iodide in the wet process, as may be proved by allowing a drop of saliva to fall on a glass plate, and then carefully removing it with a silk handkerchief. On Collodionizing the glass and passing it through the Nitrate Bath, there will be a transparent mark of defective development on that particular part, showing that the Iodide had not undergone the usual change in the Camera.

Grove's Electrical Images.—Mr. Grove has succeeded in producing latent images by electricity. In the experiments described, a plate of glass was electrized in certain parts, and then breathed on or exposed to the fumes of Hydrofluoric Acid; in either case the vapour settled exclusively upon the *non*-electrical part of the glass. When the glass was first electrized, and afterwards coated with Iodide of Silver and exposed to light, Pyrogallic Acid produced no reduction. These experiments appear to show that Light and Electricity act in opposite directions, and that the effects they produce upon Iodide of Silver neutralize each other.

Experiments of Busk and others.—Mr. Busk has lately communicated a paper to the Blackheath Photographic Society, in which he shows that ordinary writing-paper sensitized with Nitrate of Silver undergoes an invisible change when placed in contact with certain surfaces; and that in consequence of this change the paper loses its property of being darkened by exposure to light. To exhibit the phenomenon in perfection he recommends that the Nitrate bath should be rather strongly acidified with Tartaric or Acetic Acid. A few hours' contact with an engraving will then produce the effect, and those portions of the sensitive paper which have been touched by the blacks of the engraving will remain white in the solar ray, whilst the other untouched parts will darken in the usual manner.

Mr. Malone observes with reference to the above, that much depends upon the composition of the colouring-ink of the engraving, and that one kind of ink will suspend the reducing process in a sensitive paper, whilst another will fail in doing so. His mode of procedure is as follows:—The paper is rendered sensitive upon a neutral Nitrate Bath, and is then placed between the leaves of a book. Spontaneous darkening gradually ensues, but the parts opposite to the black letters remain white, in consequence of some unexplained influence exerted by the ink.

Invisible Images produced by the Agency of Ozone.—M. Thenard has shown that ordinary paper exposed to a current of ozonized oxygen, experiences a change not visible to the eye, but becoming so when the paper is laid in contact with a sensitive sheet containing Chloride and Nitrate of Silver: blackening of the Nitrate takes place opposite to the ozonized surface. When the ozonized paper is enclosed in a damp tube, a peculiar odour is gradually developed, due in all probability to an oxidation of the organic matter into a body resembling Aldehyde or Formic Acid in its property of reducing Nitrate of Silver to the metallic state. These experiments of M. Thenard were undertaken in consequence of the publication of a series of observations by M. Niépce de St. Victor, attributing similar effects to the agency of latent light. The ingenuity of M. Niépce is beyond praise, but the opinion entertained at the present time appears to be that the phenomena he has described, are susceptible of a simpler explanation than that involved in the supposition of stored-up light.

CHEMICAL NATURE OF DEVELOPED IMAGES.

Photographic pictures obtained by developing an invisible image with a reducing agent, contain usually a far larger quantity of metallic Silver than those produced by the long-continued action of light alone. Hence they are less easily injured by destructive agents, such as Cyanide of Potassium, Oxidizers, etc. The plan which has been adopted to ascertain the actual quantity of Silver present in an image, is first to convert the deposit into Chloride of Silver, and afterwards into Sulphide of Silver, by immersion in a solution of a soluble Sulphide. The more opaque the image appears after this treatment, the greater the quantity of real Silver.

Developed images vary, however, materially in their nature and properties, according to the circumstances under which they were produced. Photographic prints, for instance, taken on Chloride of Silver, by development after a moderate amount of exposure, resemble very closely images obtained by the direct action of light alone, whilst images like Collodion positives are essentially different, and do not react in the same manner with tests. The former, indeed, may be compared to images formed by direct sun-light upon Chloride of Silver combined with organic matter; but the latter to images upon *pure* Chloride of Silver, which, as before shown, consist, after fixing, of metallic Silver only. The following conditions may be mentioned as affecting the character of the developed image.

a. The Surface used to sustain the Sensitive Layer.—Albumen and Gelatine are favourable to the production of a brown and opaque image, which will bear magnifying without showing separate particles. Cyanide of Potassium and Oxidizing agents dissolve this image, and it will not amalgamate with Mercury. It is probably not metallic, but partly organic in its nature. Collodion, on the contrary, often gives a grey and slaty image, the ultimate particles of which are seen on magnifying. It amalgamates with hot Mercury, but is little affected by fixing agents and oxidizers. This image is nearly or quite metallic.

Certain organic matters may be dissolved in the Collodion, and the result will be to produce an image intermediate in properties between the two last described. Glycyrrhizine and Grape Sugar may be mentioned in illustration.

b. The Nature of the Sensitive Salt.—Bromide of Silver added to the Iodide in an Albumen or a Gelatine process, produces an image with increased opacity, and one which from the action of tests we conclude to be more organic in its nature. Bromide of Silver in Collodion, however, diminishes the intensity, and renders the image grey and metallic. In Collodion containing certain kinds of organic matter purposely added, Bromide behaves in the same manner as in Albumen, *increasing* the opacity of the developed image.

In the case of Chloride of Silver employed to receive a latent image, and supported by a surface of Gelatine or Albumen, the impression is usually slightly visible before development; and when such is the case the resulting picture will be organic in its nature, and behave with tests more in the manner of an ordinary Photographic paper darkened by light.

c. The Developing Agent employed.—This subject has already been noticed. Organic developers, Gallic and Pyrogallic Acids, tend to produce images of the opaque kind; but the inorganic protosalts of Iron, grey and metallic images. *Acetate* of Iron resembles Pyrogallic Acid in its action more than it resembles the Sulphate of Iron.

The addition of a strong acid like Nitric Acid to the developer, produces a deposit, the particles of which are large and crystalline, with small opacity by transmitted light; but an alkaline condition of the solutions is favourable to a brown deposit, with the particles in a state of fine division.

d. The stage of the Development.—The red image first formed on the application of the developer to a gelatinized or albuminized surface of Iodide of Silver is less metallic, and more easily injured by destructive tests, than the black image, which is the result of prolonging the action. Developed Photographic prints, when of a bright red colour after fixing, correspond in properties to those obtained by the direct action of light on paper prepared with Chloride of Silver, and less closely to Collodion, or even to fully developed Talbotype Negatives.

e. The intensity of the light by which the Invisible Image was formed.—A very strong light acting for a short time, is followed by the development of the red image, the particles of which are finely divided, and easily acted on by solvents and oxidizing agents. A dull light on the other hand, acting for a longer time, is succeeded by an image of the metallic variety, which amalgamates with Mercury. The two varieties of deposit may often be seen on the same picture, the former in the high lights, as the sky, the latter in the deep shadows where the chemical rays are feeble.

CHAPTER IV.

ON FIXING THE PHOTOGRAPHIC IMAGE.

A SENSITIVE layer of Chloride or Iodide of Silver on which an image has been formed, either with or without the aid of a developing agent, must pass through further treatment in order to render it indestructible by diffused light. The image itself is sufficiently permanent, and cannot be said, in correct language, to need *fixing;* but the unchanged Silver Salt which surrounds it, being still sensitive to light, tends to be decomposed in its turn, and so the picture is lost.

The list of solvents of Chloride and Iodide of Silver has been given in Chapter II., but some are better adapted for fixing than others. In order that any body may be employed with success as a fixing agent, it is required not only that it should dissolve unchanged Chloride or Iodide of Silver, but that it should produce no injurious effect upon the image. A solvent action upon the image is most liable to happen when the agency of light alone, without a developer, has been employed: in that case the darkened surface, not being reduced perfectly to the metallic state, remains soluble to a certain extent in the fixing liquid.

AMMONIA AND OTHER FIXING AGENTS.

Ammonia.—Ammonia dissolves Chloride of Silver readily, but not Iodide of Silver: hence its use is necessarily confined to the direct sun proofs upon paper. Even these however cannot advantageously be fixed in Ammonia unless a deposit of *Gold* has been previously produced upon the surface by a process of "toning," presently to be explained: an unpleasant *red tint* is always caused by Ammonia acting upon the darkened material of a sun picture as it comes from the printing-frame.

The principal objections to the use of Ammonia as a fixing agent are its pungent odour, and also the fact that it is scarcely strong enough in its affinities to dissolve the Oxide of Silver when associated with Albumen and similar bodies.

Chloride and Iodide as Fixing Agents.—The Chlorides of Potassium, Ammonium, and Sodium possess the property of dissolving a small portion of Chloride of Silver. In the act of solution a *double salt* is formed, a compound of Chloride of Sodium with Chloride of Silver, which may be crystallized out by allowing the liquid to evaporate spontaneously. The earlier Photographers employed a saturated solution of common Salt for fixing paper prints; but the fixing action of the Alkaline Chlorides is very slow and imperfect.

The Iodide of Potassium has been used as a fixing agent for Iodide of Silver. It dissolves it by forming a double salt in the manner before described.

It is important to remark in the solution of the insoluble Silver Salts by Alkaline Chlorides, Iodides, etc., that the amount dissolved is not in proportion to the *quantity* of the solvent, but to the degree of concentration of its aqueous solution. The reason is that the double salt formed is *decomposed* by a large quantity of water. Hence it is only a saturated solution of Chloride of Sodium which possesses any considerable power of fixing; and with the Iodide of Potassium the same rule holds good—the stronger the solution the more Iodide of Silver will be taken up by a given weight. The addition of water produces milkiness and a deposit of the Silver Salt previously dissolved.

HYPOSULPHITE OF SODA AS A FIXING AGENT.

Hyposulphurous Acid is one of the Oxides of Sulphur.

in mind, because this salt is liable to undergo spontaneous change into the black Sulphide of Silver, as will be shown in Chapter VIII.

The quantity of Chloride of Silver which Hyposulphite of Soda will dissolve may be stated roughly as about one-third of its weight. If the proportion of Chloride be increased to more than one-half of the Hyposulphite, there will usually be an abundant deposition of minute sparkling crystals, since the second, or sparingly soluble double salt of Hyposulphite of Silver and Soda will then be formed.

When Hyposulphite of Soda is employed as a fixing agent it is a safe precaution to convert any Nitrate of Silver which may be present into Chloride of Silver, otherwise there will be a danger of the solution becoming discoloured from a decomposition into Sulphide of Silver. This change will be explained more particularly in the Section on the fixing of paper proofs, in Chapter VIII.

Iodide of Silver is dissolved by Hyposulphite of Soda more slowly than Chloride of Silver, and the amount eventually taken up is less. This is partly due to the fact that the Iodide of Sodium which accumulates in the liquid during the solution of the Iodide of Silver exercises an opposing affinity, and checks the continuance of the process.

CYANIDE OF POTASSIUM AS A FIXING AGENT.

The chemistry of Cyanogen is sketched in Part III.

The Cyanide of *Potassium* is the salt most frequently employed in fixing, but Cyanide of Sodium will answer the purpose equally well. Cyanide of Potassium, the commercial manufacture of which is described in the Vocabulary, occurs in the form of fused lumps of considerable size. In this state it is usually contaminated with a large percentage of Carbonate of Potash, amounting in some cases to more than half its weight. By boiling in proof Spirit the Cyanide may be extracted and crystallized, but this operation is scarcely required as far as its use in Photography is concerned.

Cyanide of Potassium absorbs moisture on exposure to the air. It is very soluble in water, but the solution decomposes on keeping; changing in colour and evolving the odour of *Prussic Acid,* which is a Cyanide of Hydrogen. Cyanide of Potassium is highly poisonous, and must be used with caution.

Solution of Cyanide of Potassium is a most energetic agent in dissolving the insoluble Silver Salts; far more so than the Hyposulphite of Soda. The Salts are in all cases converted into Cyanide, and exist in the solution in the form of a soluble double Salt, which, unlike the double Iodide, is not decomposed by dilution with water. Cyanide of Potassium is not adapted for fixing positive proofs upon Chloride of Silver; and even when a developer has been used, unless the solution of the Cyanide is tolerably dilute, it is apt to attack the image, converting it superficially into Cyanide of Silver, and then dissolving it in the form of a double Cyanide of Potassium and Silver.

The solvent powers of Cyanide of Potassium on Metallic Silver are much increased by the addition of a little Iodine to its aqueous solution. A colourless liquid is formed, which has been termed "Iodo-cyanide of Potassium," but its exact composition has not been determined.

OBSERVATIONS ON THE RELATIVE AFFINITIES OF CHLORINE, IODINE, AND HYPOSULPHUROUS ACID FOR SILVER.

Hyposulphurous Acid is usually viewed as a body possessing extraordinary affinities for Silver, inasmuch as a solution of Hyposulphite of Soda decomposes both Iodide and Chloride of Silver. It may be shown, however, on the other hand, that a solution of a Chloride or an Iodide will decompose Hyposulphite of Silver under some circumstances; and hence the relative affinities are less evident than may appear. The use of these fixing agents, indeed, depends upon their being present in large excess over the Salt of Silver to be dissolved, in order that a true double salt may be formed. When two different fixing agents are employed in a state of mixture, that particular one may prevail which is present in largest quantity, even although its affinities for Silver are weaker than those of the other.

Thus although Chloride of Silver dissolves easily in solution of Hyposulphite of Soda, we find that Hyposulphite of Silver is decomposed and converted into Chloride of Silver when treated with a saturated solution of Chloride of Sodium. And the same remark applies to Iodide of Silver: it is decomposed by a large excess of Hyposulphite of Soda, but not by a small excess. The addition of Iodide of Potassium to a fixing bath of Hyposulphite nearly saturated with Silver Salt, will precipitate a portion of the Silver in the form of the yellow Iodide of Silver.

The above facts will serve as a guide in the employment of the Hyposulphite fixing bath. We must not expect to be able to dissolve the full quantity of Chloride of Silver required to produce the second or sparingly soluble compound represented by the formula AgO,S_2O_2+NaO,S_2O_2, because the accumulation of Chloride of Sodium which gradually takes place in the fixing liquid, will stop the action at a certain point. And in the case of Iodide of Silver, the fixing will be retarded in a manner even more decided, as has been already mentioned.

CHAPTER V.

THE NATURE AND PROPERTIES OF LIGHT.

resent Chapter is devoted to a discussion of the more able properties of Light; the object being to select prominent points, and to state them as clearly as le, referring, for information of a more complete o acknowledged works on the subject of Optics.

Chapter will be divided into four Sections :—first, npound nature of Light, with the Laws of refraction t; second, Lenses and the Camera; third, Actinism; , Binocular Vision and the Stereoscope.

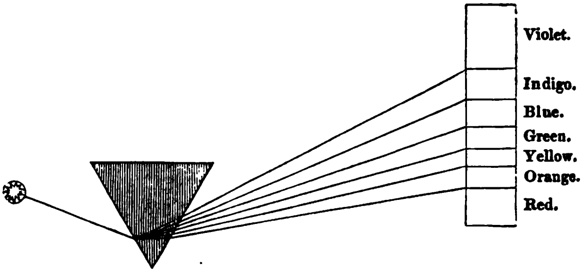
SECTION I.

The Compound Nature of Light.

ideas entertained on the subject of Light, before the f Sir Isaac Newton, were vague and unsatisfactory. shown by that eminent philosopher, that a ray of ht was not *homogeneous*, as had been supposed, but ed of several rays of vivid colours, united and inter- d.

fact may be demonstrated by throwing a pencil of ht obliquely upon one side of a *prism*, and receiving long image so formed, upon a white screen.

space illuminated and coloured by a pencil of rays ed in this way is called "the Solar Spectrum." The of a prism in decomposing white light will be more fully explained at page 70. At present we notice only that seven principal colours may be distinguished in the Solar Spectrum, viz. red, orange, yellow, green, blue, indigo, and violet. Sir David Brewster has made observations which lead him to suppose that the *primary* colours are in reality but three in number, viz. red, yellow, and blue, and that the others are *compound*, being produced by two or more of these overlapping each other; thus the red and yellow spaces intermingled constitute *orange;* the yellow and blue spaces, *green.*



The composition of white light from the seven prismatic colours may be roughly proved by painting them on the face of a wheel, and causing it to rotate rapidly; this blends them together, and a sort of greyish-white is the result. The white is imperfect, because the colours employed cannot possibly be obtained of the proper tints or laid on in the exact proportions.

The decomposition of light is effected in other ways besides that already given :—

First, by *reflection* from the surfaces of coloured bodies. All substances throw off rays of light, which impinge upon the retina of the eye and produce the phenomena of vision. Colour is caused by a *portion only*, and not the whole, of the elementary rays, being projected in this way. Surfaces termed *white* reflect all the rays; coloured surfaces absorb some and reflect others : thus *red* substances reflect only red rays, *yellow* substances, yellow rays, etc., the ray rhich is reflected in all cases deciding the colour of the ubstance.

Secondly, light may be decomposed by *transmission* hrough media which are transparent to certain rays, but paque to others.

Ordinary transparent glass allows all the rays constituing white light to pass; but by the addition of certain netallic oxides to it whilst in a state of fusion, its properies are modified, and it becomes *coloured.* Glass stained y Oxide of Cobalt is permeable only to blue rays. Oxide f Silver imparts a pure yellow tint; Oxide of Gold or uboxide of Copper a ruby red, etc.

PROPERTIES OF LIGHT.

The agency of Light produces a variety of distinct effects pon the bodies which surround us. These may be classed ogether as the properties of light. They are of three inds—the phenomena of colour and vision, of heat, and f chemical action.

By resolving white light into its constituent rays, we nd that each of these properties is associated more paricularly with certain of the elementary colours.

The *yellow* is decidedly the most luminous ray. On exmining the Solar Spectrum, it is seen that the brightest art is that occupied by the yellow, and that the light diminishes rapidly on each side. So again, rooms glazed rith yellow glass always appear abundantly illuminated, rhilst the effect of red or blue glass is dark and sombre. he yellow colour therefore constitutes that portion of rhite light by which surrounding objects are rendered isible; it is essentially the *visual* ray.

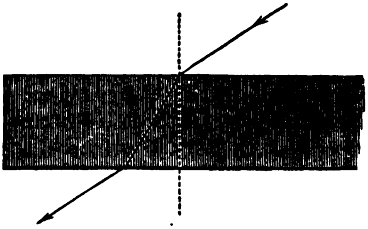
The *heating properties* of the sunlight reside principally n the red ray, as is shown by the expansion of a mercuial thermometer placed in that part of the spectrum.

The chemical action of light corresponds more to the ndigo and violet rays, and is wanting, as regards its inuence upon Iodide of Silver, both in the red and yellow. trictly speaking, however, it cannot be localized in either of the coloured spaces, as will be more fully shown in the third Section of this Chapter, to which the reader is referred.

REFRACTION OF LIGHT, AND LENSES.

A ray of light, in its passage through any transparent medium, travels in a straight line as long as the density of the medium continues unchanged. But if the density varies, becoming either greater or less, then the ray is *refracted,* or bent out of the course which it originally pursued. The degree to which the refraction or bending takes place depends upon the nature of the new medium, and in particular upon its density as compared with that of the medium which the ray had previously traversed. Hence Water refracts light more powerfully than Air, and Glass more so than Water.

The following diagram illustrates the refraction of a ray of light:—



The dotted line is drawn perpendicularly to the surface, and it is seen that the ray of light on entering is bent *towards* this line. On emerging, on the other hand, it is bent to an equal extent *away from the perpendicular,* so that it proceeds in a course parallel to, but not coincident with its original direction. If we suppose the new medium, in place of being more dense than the old, to be *less dense,* then the conditions are exactly reversed,—the ray is bent away from the perpendicular on entering, and towards it on leaving.

It must be observed that the laws of refraction apply nly to rays of light which fall upon the medium at *an ngle:* if they enter perpendicularly—in the direction of e dotted lines in the last figure—they pass straight rough without suffering refraction.

Notice also, that it is *at the surface of bodies* that the eflecting power acts. The ray is bent on entering, and ent again on leaving; but whilst within the medium it ontinues in a straight line. Hence it is evident that by ariously modifying the surfaces of refractive media the ys of light may be diverted almost at pleasure. This ill be rendered clear by a few simple diagrams.

In the figures given below the dotted lines represent erpendiculars to the surface at the point where the ray lls, and it is seen that the usual law of bending *towards* e perpendicular on entering, and *away* from it on leaving e dense medium, is in each case correctly observed.

Fig. 1.

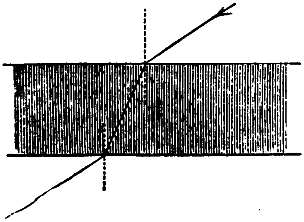


Fig. 2.

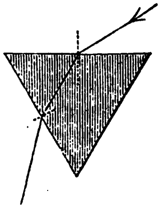


Fig. 3.

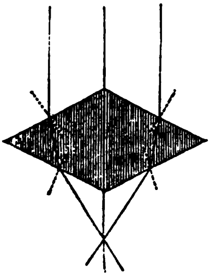


Fig. 4.

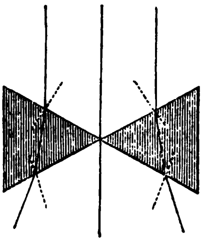


Fig. 2, in the last page, termed a prism, bends the ray permanently to one side; fig. 3, consisting of two prisms placed base to base, causes rays before parallel to meet in a point; and conversely, fig. 4, having prisms placed edge to edge, diverts them further asunder.

The various forms of Lenses.—The phenomena of the refraction of light are seen in the case of *curved* surfaces in the same manner as with those which are plane.

Glasses ground of a curvilinear form are termed *Lenses.* The following are examples.

Fig. 1.

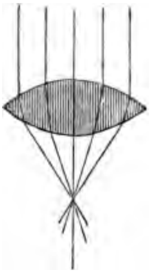


Fig. 2.

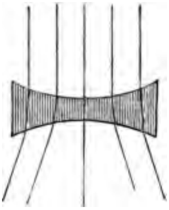


Fig. 3.

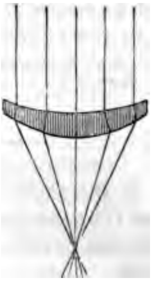


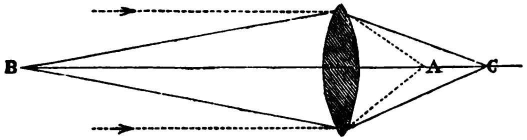
Fig. 1 is a biconvex lens; fig. 2, a biconcave lens; and fig. 3, a *meniscus* lens.

As far as regards their refractive powers, such figures may be represented, nearly, by others bounded by straight lines, and thus it becomes evident that a biconvex lens tends to condense rays of light to a point, and a biconcave to scatter them. A meniscus combines both actions, but the rays are eventually bent together, the convex curve of a meniscus lens being always greater than the concave.

The Foci of Lenses.—It has been shown that convex lenses tend to condense rays of light and bring them together to a point. This point is termed "the focus" of the Lens.

The following laws as regards the focus may be laid down:—That rays of light which are pursuing a parallel course at the time they enter the Lens are brought to a cous at a point nearer to the Lens than diverging rays. The rays proceeding from very distant objects are parallel; those from objects near at hand diverge. The sun's rays are always parallel, and the divergence of the others becomes greater as the distance from the Lens is less.

The focus of a Lens for parallel rays is termed the "principal focus," and is not subject to variation; this is the point referred to when the *focal length* of a Lens is spoken of. When the rays are not parallel, but diverge from a point, that point is associated with the focus, and the two are termed "conjugate foci."

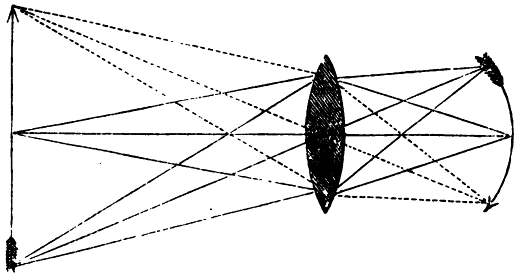


In the above diagram A is the principal focus, and B and C are conjugate foci. Any object placed at B has its focus at C, and conversely when placed at C it is in focus at B.

Therefore, although the principal focus of a Lens (as determined by the degree of its convexity) is always the same, yet the focus for objects near at hand varies, being longer as they are brought closer to the Lens.

Formation of a Luminous Image by a Lens.—As the rays of light proceeding from a *point* are brought to a focus by means of a Lens, so are they when they proceed from an object, and in that case *an image of the object* is the result.

In order that the course pursued by pencils of rays proceeding from an object may be easily traced, the lines from the barb of the arrow in the figure in the next page are *dotted.* Observe that the object is necessarily *inverted,* and also that those rays which traverse the central point of the Lens, or the centre of the *axis,* as it is termed, are not bent away, but pursue a course either coincident with, or parallel to the original, as in the case of refracting media with parallel surfaces.



Enlarged and reduced Images.—When an object is placed at some distance in front of a Lens an image is formed, smaller than the object; but if the object be advanced nearer to the Lens the image increases in size until it becomes, first equal to, and then larger than the original, the focus at the same time receding to a greater distance from the Lens.

Thus if a photographic portrait be approximated to a Lens, an image of the life size may be thrown upon a screen, just as the rays proceeding from the living model were in the first instance employed to form the portrait. The two planes, in fact, of the object and of the image are strictly *conjugate foci* (p. 67), and it is immaterial from which of the two, anterior or posterior, the rays of light proceed.

Amplifying instruments, like Woodward's Patent Solar Camera, are constructed upon the above principle, and are found useful in enlarging photographs to three or four times their original diameter. A loss of definition always results in this process, which may conveniently be remedied by the pencil of the artist.

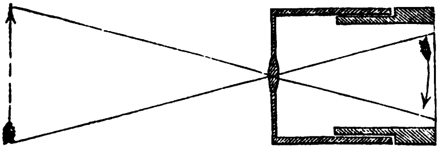
Lenses of long and short focus.—A Lens of short focus placed at a given distance from an object forms a small image, the rays being strongly refracted. If the Lens be brought nearer to the object the image becomes larger as above shown, but at a certain point the approximation must be stopped or the Lens will be *strained* as the opticians term it, and distortion will result. Therefore Lenses are purposely constructed of a longer focus when a large image is required.

Long-focus lenses for taking large pictures have usually a considerable diameter, but it will be understood that the size of a Lens has nothing whatever to do with the size of the image. *The focal length* of the Lens, at a given distance, determines the size of the image; nevertheless, since the luminous rays are diffused over a large space when the focus is long, the optician is compelled in such a case to increase the aperture of the glass in order to transmit more light.

SECTION II.

The Photographic Camera.

The Photographic Camera, in its essential nature, is an extremely simple instrument. It consists merely of a *dark chamber*, having an aperture in front in which a Lens is inserted. The accompanying figure shows the simplest form of Camera.



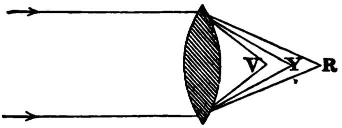
The body is represented as consisting of two sliding portions; but the same object of lengthening or shortening the focal distance may be attained by making the Lens itself movable. A luminous image of any object placed in front of the Camera is formed by means of the Lens, and received upon a surface of ground glass at the back part of the instrument. When the Camera is required for use, the object is *focussed* upon the ground glass, which is then removed, and a slide containing the sensitive layer inserted in its place.

The luminous image, as formed upon the ground glass, is termed the "Field" of the Camera; it is spoken of as being flat or curved, sharp or indistinct, etc. These and other peculiarities depending upon the construction of the Lens will now be explained.

Chromatic Aberration: Visual and Actinic Focus.—The outside of a biconvex lens resembles the sharp edge of a *prism*, and necessarily produces *decomposition* in the white light which passes through it. The luminous image of an uncorrected Lens, is in consequence bounded by coloured fringes.

The action of a prism in separating white light into its constituent rays may be simply explained. The indigo and violet rays are more bent away than the yellow and red, and consequently they are separated from them, and occupy a higher position in the Spectrum. (See the diagram at p. 62.) A little reflection will show that in consequence of this unequal refrangibility of the coloured rays, white light must invariably be decomposed on entering any dense medium obliquely. This is indeed the case; but if the surfaces of the medium *are parallel to each other* the effect is not seen, because the rays recombine on their emergence, being bent to the same extent in the opposite direction. Hence light is transmitted colourless through an ordinary pane of glass, but yields the tints of the Spectrum in its passage through a prism or a lens, where the two surfaces are inclined to each other at an acute angle.

The same causes which produce chromatic aberration in a Lens, tend also to separate the chemical from the visual

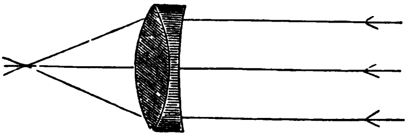


focus. The violet and indigo rays are more strongly bent in than the yellow, and still more than the red; consequently the focus for each of those colours is at a different point. The diagram in the preceding page shows this.

V represents the focus of the violet ray, Y of the yellow, and R of the red. Hence, as the chemical action corresponds more to the violet, the most marked actinic effect would be produced nearly at V. The luminous portion of the spectrum however is *the yellow,* consequently the visual focus is at Y.

Photographers have long recognized this point; and therefore, with ordinary Lenses, not corrected for colour, rules are laid down as to the exact distance which the sensitive plate should be shifted away from the visual focus in order to obtain the greatest amount of distinctness of outline in the image impressed by chemical action.

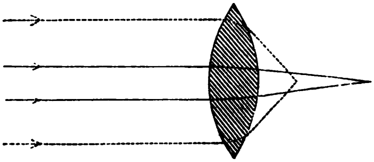
Chromatic aberration is corrected by combining two lenses cut from varieties of glass which differ in their power of separating the coloured rays. These are generally the dense flint-glass containing Oxide of Lead, and the light crown-glass. Of the two lenses, the one is *biconvex,* and the other *biconcave;* so that when fitted together they produce a compound Achromatic lens of a meniscus form, as shown in the diagram.



The first Lens in this figure is the flint- and the second the crown-glass. Of the two the biconvex is the most powerful, so as to overcome the other, and produce a total of refraction to the required extent. Each of the Lenses is made from glass of different dispersive power to that of its coadjutor; and the effect of passing the rays through both, is, by overlapping the coloured spaces, to unite the complementary tints, and to re-form white light.

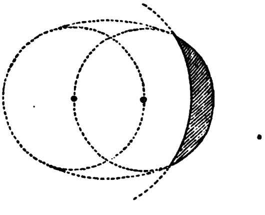
Lenses which have been properly achromatized in the way above described have their chemical and visual foci nearly coincident; and by purposely correcting the lens to a point a little higher in the spectrum it becomes perfect in that respect.

Spherical or Axial Aberration.—Spherical aberration is the property possessed by Lenses *which are segments of spheres,* of refracting rays of light unequally at different parts of their surfaces. The following diagram shows this in an exaggerated degree.



Observe that the dotted lines which fall upon the circumference of the Lens are brought to a focus at a point nearer to the Lens than those passing through the centre; in other words, the outside of the Lens refracts light more powerfully. This causes a degree of confusion and indistinctness in the image, from various rays crossing, and interfering with each other.

In correcting for spherical aberration, the first point to be attended to, is the curve of the Lens itself. A biconvex Lens, as shown in the above diagram, is the worst form. The Meniscus Lens (p. 66) is preferable, and is



usually employed. But a Lens of the shape given above, one surface of which is a section of an ellipse, and the other of a circle struck from the furthest of the two foci of hat ellipse, is the most perfect, and produces no aberration n the case of rays parallel with the axis. The difficulty of grinding such a Lens however is very great.

The process of achromatizing a Lens affords another means of correcting for spherical aberration; and it does not appear that the curves ordinarily adopted (p. 71) are the best which could be devised for avoiding spherical aberration. A meniscus of crown glass cemented to a concavo-convex of flint glass, produces a superior combination, being quite achromatic, and at the same time giving a sharp image with a comparatively large aperture.*

But spherical aberration, even in a Lens which is badly made as regards *form*, may be remedied in another way, viz. by using a diaphragm or stop, so as to cut off a portion of the light, and prevent the same pencil of rays from falling both on the centre and on the edge of the Lens. As he action of a stop is more fully explained a few pages n advance, we defer the further consideration of it for the present.

Curvature of the Field.—In using a Camera mounted with a common Meniscus Lens, it will be observed that when the centre of the field has been focussed, the outer portions of the image appear indistinct, whilst if the ground glass be pushed in a little, the outside becomes sharp, but the centre is thrown out of focus. This defect is sometimes attributed to spherical aberration, but incorrectly so, because indistinctness from that cause is seen alike at every portion of the field. The want of definition which can be remedied by shifting the position of the focussing-screen we refer rather to curvature of the field, or to the fact that the image of a flat surface, formed by a Lens, falls not upon a plane, but *on a hollow sphere*, as shown at page 68.

In the diagram of the next page the centre line running at right angles to the general direction of the Lens is the *axis;* an imaginary line, on which the Lens may be said to rotate as a wheel turns on its axle. The lines A A represent rays of light falling parallel to the axis; and the dotted lines, others which have an *oblique* direction; B and C show the points at which the two foci are formed. Observe that these points, although equidistant from the centre of the Lens, do not fall in the same vertical plane, and therefore they cannot both be received simultaneously upon the ground glass of the Camera, which would occupy the position of the perpendicular double line in the diagram.

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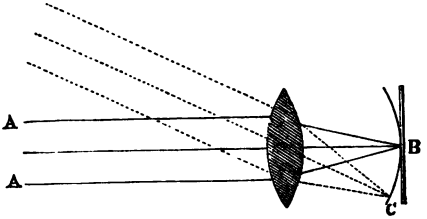
* See a paper by T. Grubb, in the 'London Photographic Journal,' vol. vi. p. 257.



The defects due to curvature of the field, might be avoided by *bending* inwards the glass or paper used to sustain the sensitive Iodide, in such a way as to meet the image: but practically this plan is not desirable. The image itself therefore must be flattened out, and this can be effected by means of the diaphragms before alluded to in the paragraph on spherical aberration: the position and use of which will be shown in the following pages.

Variation of Focus for Near and Distant Objects.—Lenses employed with the full aperture, do not render near and remote objects sharp upon the greyed glass of the Camera at the same time. If the foreground is in focus, the Lens must be thrown inwards to make the distance clear, and *vice versâ.* This is a necessary consequence of the focal plane of any object varying with the position of the object in regard to the Lens (p. 67).

The action of a diaphragm or stop, already spoken of

ıe head of " Spherical Aberration" and " Curvature
ield," is seen to still greater advantage in remedy-
lefect now complained of.

represents rays of light radiating in all directions
uminous point and falling on the entire surface of

Fig. 1.

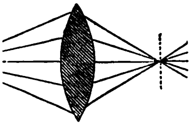


Fig. 2.

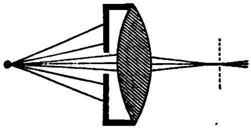


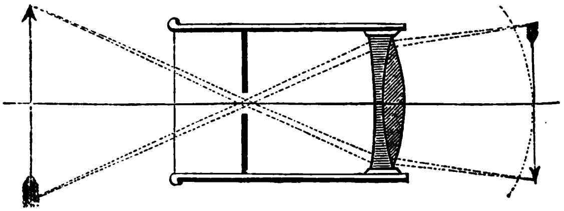
fig. 2, the action of the diaphragm in intercept-
portion of the rays which otherwise would im-
pon the outside of the glass. The focus in each
t the point where the rays cross each other after
n. Now in fig. 1 suppose the greyed screen, re-
d by the dotted line, to be advanced nearer to the
to be withdrawn from it, even in the least degree,
ge would immediately be out of focus; but in the
figure, the rays run so nearly parallel, that the ef-
slight change of position would not be perceptible.
racted pencil is as it were sharpened and drawn
that the focus has considerable *depth,* and is no
onfined to a single plane. The first figure repre-
ıat is termed *a large angular pencil* of rays, and
mall angular pencil: the latter alone can be em-
vhen near and distant objects are to be simultane-
picted.

ocal variation for near and distant objects is much
nsiderable when Lenses of very long focus are
d, and (always supposing the distance from the
o remain the same in the two cases) it becomes
lent with Lenses of short focus. Hence the small
used for stereoscopic Photography have usually
pth of focus with a comparatively large aperture.

THE SINGLE ACHROMATIC VIEW LENS.

The following diagram will serve to explain the construction of this Lens.

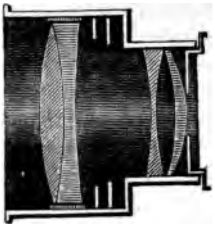
The glass is an Achromatic meniscus, placed with its concave side towards the object. In front of the Lens and at a distance from it equal to a fifth part of its focal length, are fixed a series of diaphragms, the largest being employed for subjects nearly in one plane; and the smaller for those embracing both foreground and distance.



This form of lens is dependent entirely upon the *stop or diaphragm* for correct action, and could not be used with the full aperture. For in the first place the spherical aberration is only partially overcome by the curves given to the two glasses used in achromatizing, and hence a residual error which must be corrected by the stop. Secondly, the curvature of field is so considerable, that only a small surface could be covered *flat* by the Lens of full aperture. It is for the purpose of dealing with this latter error that the diaphragms are fixed in so peculiar a position with reference to the glass. By referring to the diagram it will be seen that the effect of a stop placed at a distance in front of the Lens is to direct the oblique rays, represented in the diagram by dotted lines, through the outside portions *only* of the glass; upon which they fall at such an angle that the focus is *lengthened out*, and consequently the field instead of being concave is nearly flat. If the diaphragm were pushed in until it came in contact with the Lens, the effect would then be similar to using a ***small*** aving the same diameter as the aperture of the stop; e field of the Camera would be indistinct at the from curvature of the image. Hence the View Lens unnecessarily large and cumbrous, as might at first ; and every portion of the glass is really employed ing the picture, the centre taking the middle part, circumference of the Lens refracting the rays which d from the sides of the object.

THE ORTHOSCOPIC OR ORTHOGRAPHIC LENS.

instrument, constructed from calculations by Pro- Petzval, was proposed to supersede the old form of Lens, as giving a more truthful representation of the The name indicates the straightness of the lines ed by the Lens; but, as we shall presently show, it snomer. Nevertheless there are advantages in the graphic Lens which will secure its continued use.



above diagram is a sectional view of the Petzval scopic Lens. It has two achromatic combinations, sterior of which (consisting of a biconcave and a me- , touching at their edges) is a *dispersing* Lens (p. 66), ngthens out the focus of the rays converged by the The use of this negative or dispersing Lens consti- the peculiarity of the new instrument, and confers advantages.

he first place the Negative Lens enables the optician rcome spherical aberration without employing a small agm. This lens is not itself free from the above- defect, but the aberration is in an opposite direction to that of the first lens, consequently the two neutralize each other and the picture is sufficiently sharp.

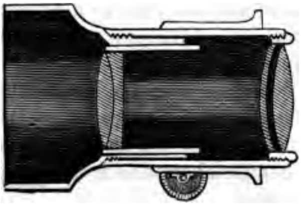
More important still is the effect which the dispersing Lens exerts in improving the oblique pencils, or those which form the outside portions of the picture. They are so far lengthened out as to lessen the concavity of the field, and to render the image sufficiently flat to fall correctly upon the focussing-screen. In this respect the Orthographic Lens is very perfect, and is universally allowed to be surpassed by none in its power of covering a large extent of surface.

Lastly, an equal intensity of light at every part of the plate, from the centre to the utmost corners, is another advantage claimed for the new Lens. If we compare it in this respect with the combination for portraits presently to be described, we find the superiority, because the picture of the Portrait Lens has only a circle in the centre where the light is full and equal, but thence to the edges the image becomes less brilliant.

Comparing the Petzval Lens with the old form as regards rapidity of Photographic action, the advantage belongs to the latter *in the case of equal apertures,* since in the orthoscopic combination a part of the light is intercepted in passing through so many glasses.

THE DOUBLE OR PORTRAIT COMBINATION OF ACHROMATIC LENSES.

The Portrait combination of Lenses is constructed to give a perfectly sharp image with an aperture of full size, and thus to ensure rapidity of action by admitting a large volume of light. The following diagram gives a sectional view.



In this combination the front Lens is an Achromatic plano-convex, with the convex side turned toward the object; and the second, which takes up the rays and refracts them further, is an achromatic Biconvex Lens; there are therefore in all four distinct glasses concerned in forming the image, which may appear at first to be an unnecessarily complex arrangement. It is found however that by combining two glasses of different curves, the aberrations of one correct those of the other to a great extent, and the field is sufficiently distinct without the employment of a diaphragm.

The manufacture of Portrait Lenses is a point of great difficulty, care being required in grinding the glasses, in order to avoid *distortion* of the image: hence the most rapid Portrait Lenses, having large aperture and short focus, are often useless unless purchased of a good maker.

The Portrait Lens however, although it produces a perfectly sharp image with the full aperture, cannot be made to embrace objects at different distances from the Camera, and the field is also more or less curved and consequently indistinct at the edges. Stops therefore are occasionally used, when length of exposure is not an object, in order to sharpen out the refracted pencils and give depth to the focus. They may be required in taking groups in a good light, or in using the Lens to copy pictures, where it is necessary to cover a plate of a full size quite up to the edge.

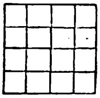
A question arises as to the proper place for a stop in a Portrait Lens, whether it should be placed in front of or between the glasses? The former position is convenient, but the latter is more correct in some instances, and by mechanical contrivances recently introduced, a diaphragm may be so placed, without removing the glasses. A stop in front of the anterior Lens diminishes the available size of the field, but renders it comparatively flat, whilst one placed between the glasses *increases* the size of the field, although leaving a little of the original curvature. In both cases the brilliancy of the image is lessened and the time of exposure prolonged, but not to so great an extent when the stop is central.

The inquiry is frequently made why the Portrait Lens gives so concave a field, since it is well known that the optician has it in his power to flatten the field very materially by altering the curves of the constituent Lenses. The answer is, that curvature of field is not esteemed a serious objection in the case of portrait lenses, because the sides of the object are usually nearer to the Lens than the centre. And it has been found that in grinding the glasses in such a way as to secure great flatness of field, the defining power of the Lens is injured as regards the oblique pencils, in consequence of the introduction of an error known as "astigmatism."

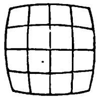
ON DISTORTION IN LENSES.

If the single Achromatic View Lens of page 76 be employed to photograph a rectangular figure like the diagram No. 1, the outside lines will be found on close inspection to be slightly curved inwards, thus producing a barrel-shaped copy, as shown in No. 2. If the Orthographic Lens of page 77 be used instead of the ordinary View Lens, the resulting photograph will be of an hour-glass shape (No. 3), the lines being bent outwards at the extremities.

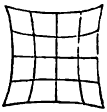
No. 1.



No. 2.



No. 3.



Observe that the central lines in each figure are perfectly straight, and that the distortion is most discernible at the edges. The larger the copy in proportion to the original the greater the distortion.

Distortion by Lenses is easily understood if we bear in mind the remarks made at page 72. The outside of the Lens refracts light more powerfully than the centre; and hence, when the whole surface of the Lens is employed to form the image, we have that confusion and overlapping which constitutes spherical aberration. To remedy this, a is so placed that the centre and the outside of the no longer co-operate, but work independently of each , and form separate portions of the image. The la- parts of the picture are then confined to the edges of ens, and as these edges refract more powerfully than entre, a bending of the rays inwards takes place, thus ituting distortion. When the stop or diaphragm ver is placed at a distance behind the Lens instead front of it, the rays cross each other *after refrac-* and thus the same bending which before produced ward distortion, now causes a distortion outwards.*

Fig. 1.

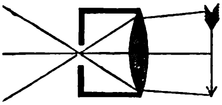
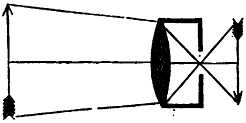


Fig. 2.



serve in the first of the above figures, which has the ragm in front, that the image of the barb of the r is formed by the *lower* edge of the Lens. In the d figure the diaphragm being placed behind the Lens, arb is formed by the *upper* edge, and thus the dis- n is in the opposite direction. In both figures those only are inserted to which the diaphragm permits a ge.

the Orthographic combination the back Lens being er than the front acts as a diaphragm to it, and hence ines are bent outwards. The distortion of the Ortho- ic Lens however is assumed not to be so great as that e old View Lens, because the diaphragm is nearer to ront glass. The distortion of an ordinary View Lens d be nearly removed if the diaphragm were pushed in it came in contact with the glass, but in that case the would be too much curved to give correct definition e margins of the picture.

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* ide 'British Journal of Photography,' vol. vi. p. 222, observations by itor.

To construct a Lens free from distortion, two glasses must be used, with the diaphragm between them. These glasses must also be both positive or condensing, and not—as in the case of the Orthographic—one condensing and the other dispersing. Amongst Lenses in ordinary use, the nearest approach to a mathematically correct instrument is the Portrait Lens, with a central stop. The front Lens of such a combination having the diaphragm behind it, produces the hour-glass distortion, whilst the back Lens, with the diaphragm in front, produces the barrel-shaped distortion. The two distortions thus tend to neutralize each other, and straighter lines are the result.

SECTION III.

On Actinism.

The term "actinism" (Gr. *ακτις*, a ray or flash) has been proposed as convenient to designate the property possessed by light of producing chemical change; the rays to which the effect is especially due being known as *actinic* rays.

If the pure Solar Spectrum formed by prismatic analysis in the manner represented at page 62 be allowed to impinge upon a prepared sensitive surface of Iodide of Silver, the latent image being subsequently developed by a reducing agent, the effect produced will be something similar to that represented in the following diagram:—

Fig. 1.

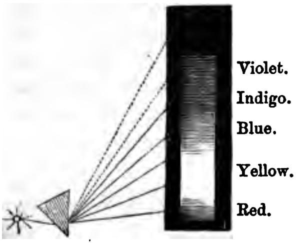


Fig. 2.

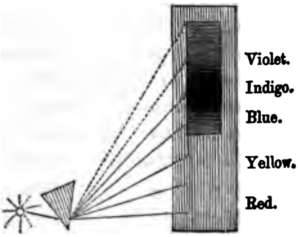


Fig. 1 shows the visible spectrum as it appears to the eye; the brightest part being in the yellow space, and the light gradually shading off until it ceases to be seen. Fig. 2 represents the effect (visible after development) of throwing the Spectrum upon Iodide of Silver. Observe that the darkening characteristic of chemical action is most evident in the upper spaces, where the *light* is feeble, and is altogether absent at the point corresponding to the bright yellow spot of the visible spectrum. The actinic and luminous spectra are therefore totally distinct from each other, and the word "Photography," which signifies the process of taking pictures by *light*, is in reality inaccurate.

To those who have not the opportunity of working with the Solar Spectrum, the following experiments will be useful in illustrating the Photographic value of different colours.

Experiment I.—Take a sheet of sensitive paper prepared with Chloride of Silver, and lay upon it strips of blue, yellow, and red glass. On exposure to the sun's rays for a few minutes, the part beneath the blue glass darkens rapidly, whilst that covered by the red and yellow glass is perfectly protected. This result is the more striking from the extreme *transparency* of the yellow glass, giving the idea that the Chloride would certainly be blackened first at that point. On the other hand, the blue glass appears very dark, and effectually conceals the tissue of the paper from view.

Experiment II.—Select a vase of flowers of different shades of scarlet, blue, and yellow, and make a Photographic copy of them, by development, upon Iodide of Silver. The blue tints will be found to act most violently upon the sensitive compound, whilst the reds and yellows will be scarcely visible; were it not that it is difficult to procure in nature pure and homogeneous tints, free from admixture with other colours, they would make no impression whatever upon the plate.

In exemplifying further the importance of distinguishing between visual and actinic rays of light, we may observe that if the two were in all respects the same, Photography must cease to exist as an Art. It would be impossible to make use of the more sensitive chemical preparations, from the difficulties which would attend the previous preparation and subsequent development of the plates. These operations are now conducted in what is termed a dark room; but it is dark only in a *Photographic* sense; being illuminated by means of yellow light, which, whilst it enables the operator easily to watch the progress of the work, produces no injurious effect upon the sensitive surfaces. If the windows of the room were glazed with *blue* in place of yellow glass, then it would be strictly a "dark room," but one altogether unfitted for the purpose intended.

In selecting glass for the Photographic dark room, considerable difference will be found in the actinic opacity of the various shades of colour. A dark orange-yellow is more impervious to chemical rays than a lighter canary-yellow, whilst a blood-red colour possesses almost perfect opacity, a Collodion sensitive plate being unaffected even by the direct rays of the sun shining through the glass. Rooms glazed with red glass, however, are extremely painful to the eyes, the retinæ being rendered for the time insensitive, and all objects assuming the complementary colour, green, on emerging into the daylight.

Another point connected with this subject of visual and actinic rays is the extent to which the sensibility of the Photographic compounds is influenced by atmospheric conditions not visibly interfering with the *brightness* of the light. It would be natural to suppose that those days on which the sun's rays are very powerful would be the best for rapid impression, but such is not by any means the case. If the light is at all of a yellow cast, however bright it may be, its actinic power will be small.

It will often be observed also in working towards the evening, that a sudden diminution of sensibility in the plates begins to be perceptible at a time when but little difference can be detected in the brilliancy of the light; the sun sinks behind a golden cloud, and all chemical action is soon at an end.

In the same manner is explained the difficulty of obtaining Photographs in the glowing light of tropical climates; the superiority of the spring months to those of the midsummer; of the morning sun to that of the afternoon, etc. April and May are usually considered the best months for rapid impression in this country; but the light continues good until the end of July. In August and September a longer exposure of the plates will be required.

THE SUPERIOR SENSIBILITY OF BROMIDE OF SILVER TO COLOURED LIGHT.

In copying the Solar Spectrum alternately upon a surface of Iodide, and Bromide of Silver, we notice a difference in the Photographic properties of these two salts. The latter is affected more extensively, to a point lower in the spectrum, than the former. In the case of the Iodide of Silver, the action ceases in the Blue space; but with the Bromide it reaches to the Green. This is shown in the following diagrams:—

Fig. 1. Fig. 2. Fig. 3.

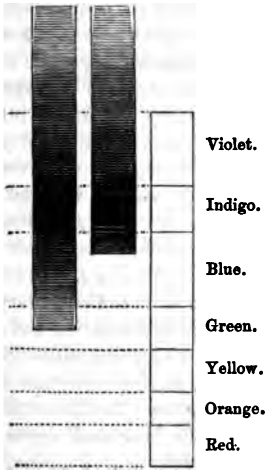


Fig. 1 represents the chemical spectrum on Bromide of Silver; fig. 2, the same upon Iodide of Silver; and fig. 3, the visible spectrum.

It might perhaps be supposed that the superior sensibility of the Bromide of Silver to green rays of light would render that salt useful to the Photographer in copying landscape scenery. It is doubtful however whether such is the case, and for the following reasons.—

A reference to the foregoing diagrams—which are shaded to represent nearly the relative intensity of the chemical action exerted by the rays at different points of the spectrum—will show that the maximum point of blackness is in the indigo and violet space, the action being more feeble in the blue space lower down; there are also highly refrangible rays extending upwards beyond the visible colours, and these invisible rays are actively concerned in the formation of the image. Hence we see that the amount of effect produced by a pure green, or even a light blue tint, upon a surface of Bromide of Silver is very small as compared with that of an indigo or violet; and since radiations of all kinds are present in copying natural objects, the green tints have not time to act before the image is impressed by the more refrangible rays.

Sir John Herschel proposed to render coloured light available in Photography by separating the actinic rays of high refrangibility, and working only with those which correspond to the blue and green spaces in the spectrum. This may be done by placing in front of the Camera a vertical glass trough containing a solution of Sulphate of Quinine. Professor Stokes has shown that this liquid possesses remarkable properties. In transmitting rays of light it modifies them so that they emerge *of lower refrangibility*, and incapable of producing the same actinic effect. Solution of Sulphate of Quinine, although appearing nearly colourless to the eye, is, if we may use the term, *opaque* to all actinic rays higher than the blue-coloured space. The proposition of Sir John Herschel above referred to was to employ a bath of Sulphate of Quinine, and having eliminated the actinic rays of high refrangibility, to work upon Bromide of Silver with those corresponding to the lower-coloured spaces. In this way he conceived that a more natural effect would be obtained.

If Photographic compounds should be discovered of greater sensibility that any we at present possess, the use of the Quinine Bath will perhaps be adopted; but at present we are compelled to trust to the superior intensity of the invisible rays for the formation of the image. In working with artificial light, such as gas or camphine, the case is different. Actinic rays of high refrangibility are comparatively wanting in gas-light, and the great bulk of the Photographic rays lie within the limits of the visible spectrum: the action is therefore more energetic upon Bromide than on Iodide of Silver.

The fact that the natural colours are not correctly represented in Photography, is often urged in depreciation of the art;—"when lights are represented by shadows," it is said, "how can a truthful picture be expected?" The insensitiveness of Iodide of Silver to the green and yellow colours occupying the lower portion of the spectrum would indeed present an insuperable difficulty *if the tints of Nature were pure and homogeneous.* Such however is not the case. Even the most sombre colours are accompanied by scattered rays of white light in quantity amply sufficient to affect the sensitive film.

This is especially seen when the coloured body *possesses a good reflecting surface*; and hence some varieties of foliage, as for instance the Ivy, with its smooth and polished leaf, are more easily photographed than others. So again with regard to drapery in the department of portraiture —it is necessary to attend not only to the colour, but also *to the material of which it is composed.* Silks and satins are favourable, as reflecting much light, whilst velvets and coarse stuffs of all kinds, if at all dark, produce very little effect upon the sensitive film.

SECTION IV.

On Binocular Vision and the Stereoscope.

An object is said to be "stereoscopic" (στερεος, solid, and σκοπεω, I see) when it stands out in relief, and gives to the eye the impression of solidity.

This subject was first explained by Professor Wheatstone in a memoir on binocular vision, published in the 'Philosophical Transactions' for 1838; in which he shows that solid bodies project different perspective figures upon each retina, and that the illusion of solidity may be artificially produced by means of the "Stereoscope."

The phenomena of binocular vision may be simply stated as follows:—If a cube, or a small box of an oblong form, be placed at a short distance in front of the observer, and viewed attentively with the right and left eye separately and in succession, it will be found that the figure perceived in the two cases is different; that each eye sees more of one side of the box, and less of the other; and that in neither instance is the effect exactly the same as that given by the two eyes employed conjointly.

A silver pencil-case, or a pen-holder, may be used to illustrate the same fact. It should be held at about six or eight inches distant from the root of the nose, and quite at right angles to the face, so that the length of the pencil is concealed by the point. Then, whilst it remains fixed in this position, the left and right eye are to be alternately closed: in each case a portion of the opposite side of the pencil will be rendered visible.

The diagrams on the next page exhibit the appearance of a bust as seen by each eye successively.

Observe that the second figure, which represents the impression received by the right eye, is more of a full face than fig. 1, which, being viewed from a point removed a little to the left, partakes of the character of a profile.

The human eyes are placed about 2½ inches, or from that to 2⅝ inches, asunder; hence it follows that, the points of sight being separated, a *dissimilar* image of a solid ob-

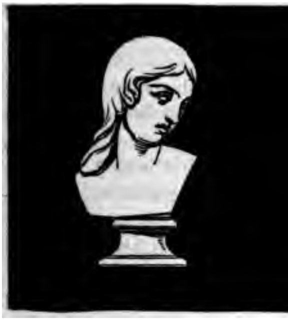


Fig. 1.

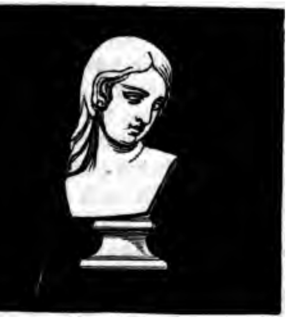


Fig. 2.

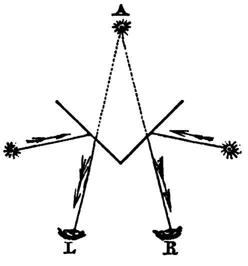
ject is formed by each eye. We do not however see *two* images, but a single one, which is stereoscopic.

In looking at a picture painted on a flat surface the case is different; the eyes, as before, form two images, but these images are in every respect similar; consequently the impression of solidity is wanting. A single picture, therefore, cannot be made to appear stereoscopic. To convey the illusion *two* pictures must be employed, the one being a right and the other a left perspective projection of the object. The pictures must also be so arranged, that each is presented to its own eye, and that the two appear to proceed from the same spot.

The reflecting stereoscope, employed to effect this, forms *luminous images* of the binocular pictures, and throws these images together, so that, on looking into the instrument, only a single image is seen, in a central position. It should, however, be understood, that no optical arrangement of any kind is indispensably required, since it is quite possible, with a little effort, to combine the two images by the unaided organs of vision. The following diagram will make this obvious:—

The circles A and B represent two wafers, which are stuck on paper at a distance of about three inches from each other. They are then viewed by *squinting* strongly, or turning the eyes inward towards the nose, until the right eye looks at the left wafer, and the left eye at the right wafer. Each wafer will then appear to become double, four images being seen, the two central of which will gradually approach each other until they coalesce. Stereoscopic pictures, arranged expressly for the purpose, may be examined in the same manner, and it will be found that the resultant solid image is formed midway, at a point where two lines, drawn across from the eyes to the pictures, cut one another. The experiment here mentioned is sometimes a painful one, and cannot easily be made if the eyes are not of equal strength; but it will serve to show that the essential principle resides in the binocular representation of the object, and not in the instrument employed to view it.

In Mr. Wheatstone's reflecting Stereoscope, *mirrors* are used. The principle of the instrument is as follows:—Objects placed in front of a mirror have their reflected images apparently *behind* the mirror. By arranging two mirrors at a certain inclination to each other, the images of the double picture may be made to approach until they coalesce, and the eye perceives a single one only. The following diagram will explain this.



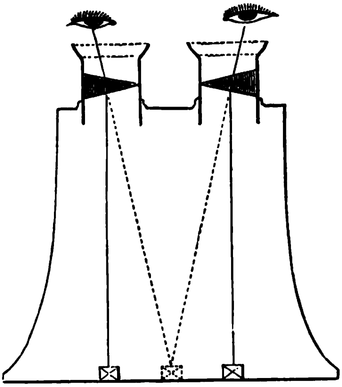
The rays proceeding from the star on either side pass in the direction of the arrows, being thrown off from the mirror (represented by the thick black line) and entering the eyes at R and L. The reflected images appear behind the mirror, uniting at the point A.

The reflecting Stereoscope is adapted principally for viewing large pictures. It is a very perfect instrument, and admits of a variety of adjustments, by which the apparent size and distance of the Stereoscopic image may be varied almost at pleasure.

The refracting Stereoscope is a more portable form of apparatus. A sectional view of the common form is given in the diagram (fig. 1).

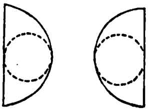
The brass tubes to which the eyes of the observer are applied contain each a semi-lens, formed by dividing a common lens through the centre and cutting each half into a circular form (fig. 2 in the following page). The half-lens viewed in section (fig. 3) is therefore of a prismatic shape, and when placed with its sharp edge as in the diagram (fig. 1), alters the direction of the rays of light proceeding from the picture, bending them outwards or away from the centre, so that in accordance with well-known

Fig. 1.



optical laws they appear to come in the direction of dotted lines in the diagram (fig. 1), and the two im coalesce at their point of junction. In the instru as it is often sold, one of the lenses is made mov and by turning it round with the finger and thumb it be seen that the positions of the images may be shift pleasure.

Fig. 2.



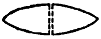


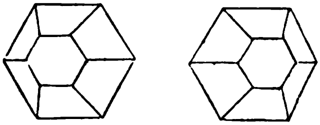
Fig. 3.

Stereoscopes are now often mounted with whole l in place of the semi-lenses above described. In that the images coalesce by an involuntary action of the of the observer. If indeed the whole lenses were set w apart than 2½ inches, it might be conjectured that v would take place principally through the inside edges that the same effect as that of a semi-lens would be duced. A single experiment, however, will suffice to that even when the centres of the lenses are exactl posite to the eyes, the two pictures combine without effort.

Rules for taking Binocular Photographs.—In vie very distant objects with the eyes, the images forme the retinæ are not sufficiently dissimilar to produce a Stereoscopic effect; hence it is often required, in taking ocular pictures, to separate the Cameras more widely the two eyes are separated, in order to give a sufficien pearance of relief. Mr. Wheatstone's original direc were, to allow about one foot of separation for each tw five feet of distance; but considerable latitude may be mitted.

If the Cameras are not placed far enough apart, the dimensions of the stereoscopic image from before backwards will be too small,—statues looking like bas-reliefs, and the circular trunks of trees appearing oval, with the long diameter transverse. On the other hand, when the separation is too wide, the reverse obtains,—objects for instance which are square, assuming an oblong shape pointing towards the observer.

To understand the cause of this, the following law in optics should be studied:—"The *distance* of objects is estimated by the extent to which the axes of the eyes must be converged to view them." If we have to turn our eyes strongly inwards, we judge the object to be near; but if the eyes remain nearly parallel, we suppose it to be distant.



The above figures represent six-sided truncated pyramids, each with its apex towards the observer, the centres of the two smaller interior hexagons being more widely separated than those of the larger exterior ones. By converging the eyes upon them so as to unite the central images in the manner represented in page 90 a greater amount of convergence will be required to bring together the two summits than the bases, and hence the summits will appear nearer to the eye; that is to say, the resultant central figure will acquire the additional dimension of *height*, and appear as a solid cone, standing perpendicularly upon its base: further, the more widely the summits are separated in relation to the bases, the taller will the cone be, although a greater effort will be required to combine the figures.

Binocular Photographs taken with too much separation of the Cameras, are distorted from a similar cause,—so strong a convergence being required to unite them that certain parts of the picture appear to approach near to the eye; and the depth of the solid image is increased.

This effect is most observable when the picture embraces a variety of objects, situated in different planes. In the case of views which are quite distant, no near objects being admitted, the Cameras may be placed with especial reference to them, even as far as twelve feet apart, without producing distortion.

It is sometimes observable, in looking at Stereoscopic pictures, that they convey an erroneous impression of the real size and distance of the object. For instance, in using the large reflecting Stereoscope, if, when the adjustments have been made and the images properly united, the two pictures be moved slowly forward, the eyes remaining fixed upon the mirrors, the Stereoscopic image will gradually change its character, the various objects it embraces appearing to become diminished in size, and approaching near to the observer: whilst if the pictures be pushed *backwards*, the image will enlarge and recede to a distance. So, again, if an ordinary slide for the lenticular Stereoscope be divided in the centre, and—looking into the instrument until the images coalesce—the two halves be slowly separated from each other, the solid picture will seem to become larger and to recede from the eye.

It is easy to understand the cause of this. When the pictures in the reflecting Stereoscope are moved *forwards*, the convergence of the optic axes is increased: the image therefore appears *nearer*, in accordance with the last-mentioned law. But to convey the impression of proximity to an object is equivalent to an apparent diminution in its size, for we judge of the dimensions of a body very much in relation to its supposed distance. Of two figures in bronze or marble, for instance, appearing of the same height, one known to be a hundred yards off might be considered colossal, whilst the other, obviously near at hand, would be viewed as a statuette.

These facts, with others not mentioned, are of great interest and importance, but their further consideration does not fall within the bounds originally prescribed to us. The practical details of Stereoscopic Photography have been arranged in a distinct Section, and will be found included in the Second Part of the Work.*

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* For a more full and detailed explanation of the Stereoscopic phenomena, see an abstract of Professor Tyndall's lectures in the third volume of the 'Journal of the Photographic Society.'

CHAPTER VI.

ON COLLODION AND THE NITRATE BATH.

IN the preceding part of this Work the physical and ch mical properties of Chloride and Iodide of Silver have be described, together with the changes which they experien by the action of Light. Nothing however has been said the surface used to support the Iodide of Silver, and to e pose it in a finely divided state to the influence of the a tinic radiation. This omission will now be supplied.

The sensibility of Iodide of Silver upon Collodion greatly superior to that of the same salt employed in co junction with any other vehicle at present known. T causes of this superior sensitiveness, as far as ascertaine may be referred to the state of *loose coagulation* of the fil and to the negative properties of the Collodion itself. must however be allowed that there are many points affe ing the sensitiveness of Iodide of Silver, both mechani and chemical, of the nature of which we are ignorant.

SECTION I.

Collodion.

Collodion (so named from the Greek word κολλαω, stick) is a glutinous, transparent fluid, prepared by d solving *Pyroxyline* in a mixture of Ether and Alcoh It was originally used for surgical purposes only, bei smeared over wounds and raw surfaces, to preserve the from contact with the air by the tough film which it leaves on evaporation.

The constituents of Photographic Collodion are three, viz..the Pyroxyline; the fluids used to dissolve it; and the iodizing compounds. Each of these will be treated in succession.

CHEMISTRY OF PYROXYLINE.

Pyroxyline is Cotton or Linen which has been altered in composition and properties by treatment with certain acids.

Cotton and Linen, when examined by the microscope, are seen to consist of fibres, and these fibres have a constant composition, containing three elementary bodies, Carbon, Hydrogen, and Oxygen, united in fixed proportions. To the combination the term *Lignine* or *Cellulose*[*] has been applied.

Cellulose is a definite chemical compound, in the same sense as Starch or Sugar, and when treated with various reagents, exhibits properties peculiar to itself. It is insoluble in most liquids, such as Water, Alcohol, Ether, etc., and also in dilute acids; but when acted upon by *Nitric Acid* of a certain strength it dissolves.

Preparation of Pyroxyline.—If, instead of treating Cotton with Nitric Acid, a mixture of Nitric and Sulphuric Acid in certain proportions be used, the effect is peculiar. The fibres contract slightly, but undergo no other visible change. On experimenting further, however, the *properties* of the cotton are found to have been affected. Its weight has increased by more than one-half; it has become soluble in various liquids, such as Acetic Ether, Ether and Alcohol, etc., and on contact with flame, it no longer burns quietly, but *explodes* with greater or less violence.

To produce the peculiar change by which Cotton is converted into Pyroxyline, both Nitric and Sulphuric Acid are employed; but the former plays the most important part. On analyzing Pyroxyline, an Oxide of Nitrogen only one step removed from Nitric Acid is detected in it, but no Sulphuric Acid. One principal use of the latter substance is to prevent the Nitric Acid from dissolving the Pyroxyline, and to produce a higher degree of concentration by absorbing a portion of the water.

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[*] Lignine and Cellulose are not precisely the same. The latter is the material composing the cell-wall; the former, the contained matter of the cell.

The property possessed by Sulphuric Acid of removing water from other bodies, may be illustrated by filling a small vessel of any kind to about two-thirds with Oil of Vitriol, and setting it aside for a few days; at the end of that time, and especially if the atmosphere be damp, it will have absorbed sufficient moisture to cause it to flow over the edge.

Now even the strongest reagents employed in chemistry contain, almost invariably, water in greater or lesser quantity. Pure Anhydrous Nitric Acid is a white, solid substance: and the liquid usually sold under that name is an *aqueous solution.* The effect therefore of mixing strong Oil of Vitriol with commercial Nitric Acid is to remove water in proportion to the amount used, and to produce a liquid containing Nitric Acid in a high state of concentration, and Sulphuric Acid more or less diluted. This liquid is the *Nitro-Sulphuric Acid* employed in the preparation of Pyroxyline.

Commercial Nitric Acid is so variable in composition, that it is often found desirable to substitute Nitrate of Potash for it in making a Nitro-Sulphuric Acid of a definite strength. When strong Sulphuric Acid is poured upon Nitrate of Potash in a state of fine powder, a solution is obtained containing Sulphate of Potash dissolved in Sulphuric Acid, and free Nitric Acid. The reaction may be thus represented:—

Nitrate of Potash *plus* Sulphuric Acid in excess
= Bisulphate Potash *plus* Nitro-Sulphuric Acid.

Constitution of Pyroxyline.—This was first determined by Hadow, in a paper communicated to the Chemical Society, and published in their Journal. Previous to that time Pyroxyline was considered by many to be a Salt of

Nitric Acid, a *Nitrate of Lignine.* This view however is erroneous, since it can be shown that the substance present is not Nitric Acid, but the *Peroxide of Nitrogen,* intermediate in composition between Nitrous Acid (NO_3) and Nitric Acid (NO_5). Peroxide of Nitrogen (NO_4) is a gaseous body of a dark red colour; it possesses no acid properties, and is incapable of forming a class of salts. In order to understand in what state this body is combined with cotton fibre to form Pyroxyline, it will be necessary to explain briefly the *Law of Substitution.*

By the careful study of the action of Chlorine, and of Nitric Acid, upon various organic substances, a remarkable series of compounds has been discovered, containing a portion of Chlorine or of Peroxide of Nitrogen in the place of Hydrogen. The peculiarity of these substances is, that they strongly resemble the originals in their physical, and often in their chemical properties. It might have been supposed that agents of such active chemical affinities as Chlorine and Oxide of Nitrogen would, by their mere presence in a body, produce a marked effect; yet it is not so in the case before us. The primitive type or constitution of the substance modified remains the same, even the crystalline form being often unaffected. It seems as if the body by which the Hydrogen is displaced had stepped in quietly and taken up its position in the framework of the whole without disturbance. Many compounds of this kind are known; they are termed by chemists "substitution compounds." The law invariably observed is, that the substitution takes place *in equal atoms:* a single atom of Chlorine, for instance, displaces one of Hydrogen; two of Chlorine displace two of Hydrogen, and so on, until, in some cases, the whole of the latter element is separated.

In illustration of these remarks, take the following instances:—Acetic Acid contains Carbon, Hydrogen, and Oxygen; by the action of Chlorine the Hydrogen may be removed in the form of Hydrochloric Acid and an equal number of atoms of Chlorine be substituted. In this way a new compound is formed, termed *Chloracetic Acid*, resembling in many important particulars the Acetic Acid itself. Notice particularly that the peculiar properties characteristic of Chlorine are completely masked in the substitution body, and no indication of its presence is obtained by the usual tests! A soluble *Chloride* gives with Nitrate of Silver a white precipitate of Chloride of Silver, unaffected by Acids, but the Chloracetic Acid does not; hence it is plain that the Chlorine exists in a peculiar and intimate state of combination different from what is usual.

Pyroxyline affords another illustration of the Law of Substitution. Omitting, for the sake of simplicity, the *number* of atoms concerned in the change, the action of concentrated Nitric Acid upon ligneous fibre may be thus explained:—

$$\text{Cotton } \textit{or} \left\{\begin{array}{l}\text{Carbon}\\ \text{Hydrogen}\\ \text{Hydrogen}\\ \text{Oxygen}\end{array}\right. + \text{ Nitric Acid}$$

equals

$$\text{Pyroxyline } \textit{or} \left\{\begin{array}{l}\text{Carbon}\\ \text{Hydrogen}\\ \text{Peroxide Nitrogen}\\ \text{Oxygen}\end{array}\right. + \text{ Water.}$$

Or in symbols:—

$$CH_nO+NO_5=C\,(H_{n-1}NO_4)\,O+HO$$

By a reference to the formula, it will be seen that the fifth atom of Oxygen contained in the Nitric Acid takes one of Hydrogen, and forms an atom of Water; the NO_4 then steps in, to fill the gap which the atom of Hydrogen has left. All this is done with so little disturbance that even the fibrous structure of the cotton remains as before.

Various forms of Pyroxyline.—There are *varieties* of Pyroxyline, depending upon the strength of the Nitro-Sulphuric Acid employed in its preparation. The first of these is the most explosive Gun Cotton. This kind of Pyroxyline contains the largest amount of Peroxide of Nitrogen; it dissolves *only in Acetic Ether*, and is left on evaporation as a white powder. It is produced by the strongest Nitro-Sulphuric Acid which can be made.

The Pyroxyline used by Photographers is formed by a Nitro-Sulphuric Acid slightly weaker than the last, and contains a smaller percentage of Peroxide of Nitrogen. It is less explosive than Gun Cotton, and dissolves not only in Acetic Ether, but also in a mixture of Ether and Alcohol.

A form of Pyroxyline, not used in Photography, resembles *Xyloidine*, the substance produced by treating starch with Nitric Acid. It is lower on the scale than the others, and contains less of Peroxide of Nitrogen. It dissolves in Acetic Ether, in Ether and Alcohol, and in Acetic Acid. The ethereal solution leaves, on evaporation, an *opaque* film, which is highly combustible, but not explosive.

By bearing in mind the properties of these compounds, which will be found more carefully described in the Vocabulary, Part III., Art. Pyroxyline, many of the anomalies complained of in the manufacture of Pyroxyline disappear. If the Nitro-Sulphuric Acid employed is too strong, the product will be insoluble in Ether; whilst if it be too weak, the fibres will be gelatinized and partly dissolved by the Acids in the form of Xyloidine.

Parchmentizing action of Oil of Vitriol upon Cellulose.—Photographic Pyroxyline is found to vary in its physical properties in a manner which can only be explained by studying a peculiar effect exercised by dilute Sulphuric Acid upon cotton fibre.

To demonstrate this action, ordinary blotting-paper is floated for a few seconds upon Oil of Vitriol previously diluted with half its bulk of water and allowed to cool: it is then abundantly washed and hung up to dry. The Sulphuric Acid must not be too strong, or it will char the paper, nor too weak, lest it cause partial conversion into dextrine and consequent solution. If it be of the right strength (sp. gr. 1·68), the paper shrinks considerably, and acquires the toughness and general appearance of parchment. It will support a heavy weight without tearing, and is so close in texture as to be almost impermeable by liquids.

Its chemical properties are the same as those of ordinary paper, and analysis fails to detect any difference in composition. When acted on by Nitric Acid this material is converted into Pyroxyline in the usual way, the Collodion film possessing the characteristic toughness and close texture of the artificial parchment itself.

With these facts before us we can readily understand that a mixture like the Nitro-Sulphuric Acid used in making Pyroxyline, at the same time that it forms a substitution compound containing Peroxide of Nitrogen, must also tend to *parchmentize* the fibre of the cotton to a greater or less extent. This is indeed the case, and by altering the relative proportions of the two acids in the mixture and increasing or diminishing the quantity of Water, the action can be regulated at will, and modifications produced which are highly useful in the manufacture of Collodion. We shall also find as we proceed that the *temperature* of the Nitro-Sulphuric Acid at the time of immersing the cotton affects the action of the acids, and consequently the properties of the resulting pyroxyline, as was shown by Mr. Hadow in his original memoir.

THE SOLUTION OF PYROXYLINE IN ETHER AND ALCOHOL, OR "COLLODION."

Pyroxyline is freely soluble in Acetic Ether, but this liquid is not adapted for the purpose required, inasmuch as on evaporation it leaves the Pyroxyline in the form of a white powder, and not as a transparent layer.

The rectified Ether of commerce has been found to answer better than any other substance as a solvent for Pyroxyline.

If the sp. gravity be about ·750, Ether contains invariably a small proportion of *Alcohol*, which appears to be necessary; the solution not taking place with absolutely pure Ether. The Pyroxyline, if properly prepared, begins almost immediately to gelatinize by the action of the Ether, and is soon completely dissolved. In this state it forms a slimy solution, which, when poured out on a glass plate, dries up into a horny transparent layer.

In preparing Collodion for Photographic purposes, we find that its physical properties are liable to considerable variation. Sometimes it appears very thin and fluid, flowing on the glass almost like water, whilst at others it is thick and glutinous. These differences relate not only to the quality of the Pyroxyline itself as shown in the last page, but also to the proportions of the Solvents employed.

When the Ether is in large excess, the film is inclined to be strong and tough, so that it can often be raised by one corner and lifted completely off the plate without tearing. It is also very contractile, and a portion of the Collodion poured on the hand draws together and puckers the skin as it dries.

These properties, produced by Ether in large proportion, disappear entirely on the addition of more Alcohol. The transparent layer is now soft and easily torn, possessing but little coherency; and this is still more manifest when the Alcohol contains water.

To appreciate the action of water in Collodion, add a few drops purposely; the Pyroxyline will be precipitated in flakes to the bottom of the bottle. On agitation the precipitate redissolves, but the Collodion is rendered glutinous, and the film left on evaporation is no longer homogeneous and transparent, but semi-opaque, reticulated or honeycombed, and so rotten that a stream of water projected upon the plate, washes it away.

Commercial Spirit of Wine often contains water in some quantity, and when such is the case, the proportion of Ether in the Collodion must be very much increased. Collodion made in this way is often highly fluid and structureless at first, adhering to the glass with some tenacity and having a short texture; but it tends to become rotten when used to coat many plates successively, the water on account of its lesser volatility accumulating in injurious quantity in the last portions.

CHANGES IN COLLODION AFTER IODIZING.

Collodion iodized with the Iodide of Potassium, Ammonium, Magnesium, or Zinc, soon assumes a yellow tint, which in the course of a few days or weeks, deepens to a full brown. This gradual coloration is due to a development of free Iodine, by a peculiar action of the Ether, which is a fluid very prone to decomposition.

Ether may, with proper precautions, be preserved for a long time in a pure state, but on exposure to the joint action of air and light it undergoes a slow process of oxidation, attended with formation of Acetic Ether and a peculiar principle resembling in properties *ozone*, or Oxygen in an allotropic and active condition. Iodide of Potassium or Ammonium is decomposed by Ether in this state, the ozonized substance liberating Iodine, which dissolves and tinges the liquid yellow.

Ether containing Pyroxyline dissolved, tends to assume the above state more quickly than pure Ether, and especially so when the Pyroxyline has undergone decomposition, and set free a portion of the Peroxide of Nitrogen. It is therefore of the utmost importance that plain Collodion should be kept in a cool place, and especially that it should never be exposed to light; even ordinary daylight will, in the course of ten days or a fortnight, confer this property of striking an immediate colour on the addition of the iodizer.

The straw-yellow colour which usually follows in the course of an hour or so after iodizing Collodion, is due to the ozonization of the Ether above described, but the further increase of that colour on keeping the Collodion for several weeks is more dependent upon the Pyroxyline; for if the Pyroxyline be omitted from the solution, and the Iodide added to the Ether and Alcohol simply, then the development of free Iodine proceeds very slowly. The rate of change under the decomposing effect of Pyroxyline is mainly affected by the stability of the particular Iodide which is employed. Iodide of Ammonium is the least stable of the iodides, and Iodide of Cadmium the most so; Iodide of Potassium being intermediate. Collodion iodized with Iodide of Cadmium usually remains nearly colourless to the last drop, if made with pure Ether, and kept in a cool and dark place.

As the presence of free Iodine in Collodion affects its photographic properties, it may sometimes be necessary to remove it. This is done by inserting a strip of Silver foil; which decolorizes the liquid, by forming Iodide of Silver, soluble in the excess of Alkaline Iodide (p. 56). Metallic Cadmium and Metallic Zinc have the same effect. Metallic Mercury also decolorizes brown Collodion, but the Protoiodide of Mercury formed has the effect of lessening the sensitiveness of the film to light.

FURTHER OBSERVATIONS ON THE MANUFACTURE OF PHOTOGRAPHIC COLLODION.

In order to conduct the manufacture of Collodion with success, a number of minor points must be considered, which could not conveniently be included in the general description given above. These relate not only to the Pyroxyline, but also to the Solvents, and the iodizing compounds: they will now be explained, type of a smaller size being employed for the sake of distinction.

The most important point is the composition of the Nitro-Sulphuric Acid, in which the Pyroxyline is prepared; for it will be found that the slightest variation in the quantity of water; in the relative proportions of the two constituent acids; or in the temperature at the time of putting in the Cotton, will affect the result. It will be advisable therefore to examine these matters separately, and in addition to speak of the condition of the fibre itself, which is important both chemically and mechanically.

a. *Effect of varying the proportion of Water in the Nitro-Sulphuric Acid.*—When many separate quantities of Pyroxyline are made in the same Nitro-Sulphuric Acid, the mixture becomes gradually weaker by the abstraction of the elements of water from the fibre, and each successive portion of Pyroxyline is less in the state of explosive Gun Cotton, and more in that of Xyloidine, than the one which preceded it.

There is considerable difference in the physical properties of Collodions made from strong and weak samples of Pyroxyline prepared as above described. In the first instance, when the product is only one step removed from Gun Cotton, the Collodion pours slowly upon the glass, and tends to thicken at the edges. The film is not very adherent, and will sometimes split away on drying. In attempting to coat a large plate, a wavy appearance, often known as *woolliness* of the film, is seen at the lower corner. With Pyroxyline made in weak acids, on the other hand, the Collodion is more limpid and free from structure, the film of Iodide when formed in the Bath presenting an even appearance throughout.

When the amount of water in the Nitro-Sulphuric Acid is carried still further, one of two things happens; either the Cotton instantly dissolves in the acid, or it is more or less disintegrated without actually dissolving. The product in the latter case is not entirely soluble in Ether and Alcohol, but leaves behind a residue consisting in part of unaltered Cotton fibre. The portion which is taken up by the Ethereal Solvent, may be considered as nearly corresponding to the lowest substitution compound "Xyloidine," and very commonly the solution of this Xyloidine leaves behind an opaque film on evaporation.

Here it may be proper to explain the reason why a weak Nitro-Sulphuric Acid sometimes dissolves the Cotton, and sometimes merely disintegrates it. Supposing the temperature, and the Cotton used, to be the same, yet the solvent action of the acids will vary with the relative proportions of Sulphuric and Nitric Acid present, even although the amount of water be correctly adjusted to that of the Sulphuric Acid. Thus a warm diluted Nitric Acid used alone acts upon the Cotton rapidly and dissolves it; but if a very small portion of diluted Sulphuric Acid be added, the tendency to dissolve the Cotton is lessened, or if the Cotton be already dissolved the diluted Sulphuric Acid throws it down again. If however the proportion of the diluted Sulphuric Acid be very considerably increased, until it reaches to as much as three times the bulk of the diluted Nitric Acid, then the tendency to dissolve the Cotton becomes greater than in the case of a mixture containing equal volumes of the two diluted acids.

b. *A peculiar action of the Oil of Vitriol in the Process.*—To demonstrate this, take a sheet of ordinary bibulous paper, and having cut it into separate pieces, float them upon Sulphuric Acid diluted with half its bulk of water and cooled: allow five seconds for the first, ten for the second, twenty for the third and so on, until the last piece is gelatinized and dissolved; then remove the Sulphuric Acid carefully by washing, and convert them into Pyroxyline. A marked difference will be perceptible between the samples of Collodion so obtained. The first noticeable effect of the previous parchmentizing, will be an increased fluidity and freedom from structural lines. The Collodion when poured upon a glass sets very rapidly, and with such firmness that the finger may be rubbed backwards and forwards without disturbing it. The film on lifting from the Bath soon becomes partially surface-dry, and repels developers or fixing agents; when washed with water and dried, it forms a dense and highly-varnished surface nearly impenetrable by liquids. The moist film after development with Pyrogallic Acid and fixing, appears unusually *tough*, and will bear pumping on without injury. It is also very contractile, and tends to draw itself away from the edges of the glass. When pushed aside it can be pulled back again like the finger of a glove. The fixing agent never removes any portion of the image from this Collodion because the Iodide of Silver is *in* the film and not only upon its surface.

The above-mentioned properties, imparted by the preliminary action of Oil of Vitriol, are not seen to an equal extent in all the pieces of paper used in the experiments, but are more decidedly evident in proportion as the acid was allowed to act for a longer time. If however the action of the acid be carried to that point at which the paper begins to soften and become semi-gelatinous, then the resulting Collodion will be entirely different, the film being rotten and powdery. This we shall presently show to be due to a disintegration by the Nitric Acid contained in the Nitro-Sulphuric Acid; which disintegration is exhibited more strongly when the fibre is previously changed, nearly into dextrine, by the prolonged action of Sulphuric Acid.

In addition to these effects produced by parchmentizing the fibre in different degrees before converting it into Pyroxyline, there are others which deserve notice. The solubility of the product in Ether and Alcohol is much increased, so that the exact amount of water in the Nitro-Sulphuric Acid becomes a point of less importance as affecting solubility, and an acid strong enough to make ordinary paper explosive and insoluble, answers perfectly in the case of paper previously parchmentized.

To secure the parchmentizing action in the ordinary process of making Pyroxyline, the amount of diluted Sulphuric Acid present in the Nitro-Sulphuric Acid should be considerably greater than that of the Nitric Acid. The Cotton then shrinks into a small compass, and the resulting Collodion will be tough and strong. The action of the Oil of Vitriol in the process evidently precedes that of the Nitric Acid, since we find that cotton fibre which has once been converted into Pyroxyline is no longer affected by diluted Sulphuric Acid, even when immersed for several hours.

A peculiar action of the Nitric Acid in the process of making Pyroxyline.—The proper action of Nitric Acid in this process is, as before shown, to communicate Peroxide of Nitrogen to the fibre, and so to convert the Cellulose into Pyroxyline; the stronger the Nitric Acid, the greater the amount of peroxide imparted. We notice, however, another action of Nitric Acid upon Pyroxyline, by which the properties of the latter are much altered. This second or modifying action, if we may so term it, is exerted not so much by a concentrated, as by a diluted Nitric Acid, and more by a hot Nitric Acid than by the same acid employed cold. To exhibit this secondary action of Nitric Acid, take ordinary Pyroxyline made by the formulæ given in the Second Part of this Work, and dip it for an instant in Nitric Acid of sp. gr. 1·45, mixed with a third of its bulk of Sulphuric Acid (to prevent it from dissolving the cotton) and heated to about 140° or 150° Fahrenheit.* The following are the main characteristics of Collodion prepared from Pyroxyline so treated:—It does not set rapidly upon the glass like the parchmentized Collodion last described, but remains liquid for a minute, or even longer, after which it rubs under the finger in a soapy manner, instead of bearing friction without injury. After passing through the bath the film is creamy, retains its surface moisture for an unusually long time, and on washing with water and drying presents a porous surface, quite lustreless, and without any varnished appearance. This film, when wet, will not bear pumping on, but is so rotten that a small stream of water allowed to impinge upon it makes a round hole. The Collodion is non-contractile, and so far from admitting of being pushed backwards and forwards after fixing with the Hyposulphite, it at once breaks away in short pieces under such treatment. Fixing agents will often remove the image from a Collodion of this kind, because the Iodide of Silver is not imprisoned by the Pyroxyline, but lies loosely upon its surface.

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* In addition to this modified Pyroxyline produced by hot Nitric Acid mixed with a little Sulphuric Acid, a remarkable change of properties may be produced by the pure Nitric Acid of 1·45 employed cold, and without any admixture of Sulphuric Acid. The Pyroxyline gradually becomes opaque, and loses its solubility in Ether and Alcohol; eventually it dissolves in the cold Nitric Acid without any evolution of gas, and if water be then added, opaque white flakes are thrown down, which, when treated with Ether and Alcohol, simply swell up without passing into solution.

Here we repeat the remark before made when speaking of the action of Sulphuric Acid, viz. that the secondary or disintegrating action of Nitric Acid is always greater when the parchmentizing effect has been previously produced; and we may also anticipate an observation to be made a few pages in advance, by adding that one kind of cellulose, such as flax, may be disintegrated by the Nitric Acid more readily than another, viz. cotton.

To secure the full disintegrating action of weak Nitric Acid in the ordinary process of preparing Pyroxyline, the bulk of Nitric Acid present in the Nitro-Sulphuric Acid should be at least equal to that of the Sulphuric Acid, and may with advantage be many times greater. The cotton will then assume an opaque appearance on being dipped in the mixture, and the Collodion will lack those properties of strength and toughness before referred to.

Composition, by volume, of Nitro-Sulphuric Acid for preparing Photographic Pyroxyline.—The following table—

	Oil of Vitriol, 1·845 at 60° F.	Pure Nitric Acid, 1·45 at 60° F.	Water.
No. 1	3	1	$\frac{7}{8}$
No. 2	2	1	$\frac{5}{8}$
No. 3	1	1	$\frac{5}{16}$
No. 4	1	2	$\frac{5}{32}$
No. 5	1	3	0

exhibits the composition of five different mixtures of Sulphuric and Nitric Acid, in which an attempt has been made to graduate the proportion of water in such a way that the percentage of Peroxide of Nitrogen imparted to immersed cotton fibre may be nearly the same in each: the table was constructed by simple experiment, taking care in each case to work with the maximum quantity of water, and stopping the addition of water only when it was found that the product left a thick sediment on being dissolved in Ether and Alcohol.

One hundred grains of purified and dried cotton immersed in either of these five mixtures, with the precautions necessary to prevent any loss from solution, ought to weigh one hundred and sixty grains: the Pyroxyline in each case is soluble, to a great extent, in glacial Acetic Acid, and also in boiling absolute Alcohol; whilst the resulting Collodion does not produce an entirely opaque film. The substitution body formed is therefore above compound D, or Xyloidine, but not above compound C (see the Vocabulary, art. PYROXYLINE). A more careful examination seems to indicate that if there be a difference in the strength of the mixtures given in the above table, No. 1 is somewhat stronger than No. 5.* The Collodion however from No. 1 is more fluid than that from No. 5, thus showing that in addition to high temperature and dilution of the mixture with water, an excess of Sulphuric Acid has to do with flowing properties of Collodion. A greater amount of fluidity than exists even in the Collodion from No. 1 may be produced by dipping the Pyroxyline first in No. 1, to secure the full action of the Sulphuric Acid, and afterwards in No. 5; the weak Nitric Acid will then act more decidedly than it would have done upon a product produced by one immersion.

The temperature employed for the above table of acids may be 150° Fahr.; and, in making the Pyroxyline, we find that the lower numbers give a product which has an opaque appearance; whereas the Pyroxyline made by Nos. 1 and 2 exhibits no opacity. The five samples of Collodion differ very much in the rapidity with which they set upon the glass, and also in their physical structure: the first setting rapidly and producing a horny film; the last scarcely possessing any power of setting. The only way of overcoming this, and putting them on something like a par, is by varying the proportions of Ether and Alcohol in the solvents, using more Alcohol in the former, and more Ether in the latter. Observe, however, that although the lower members of the series in the above table ought to yield a Collodion setting less rapidly upon the glass than the upper members, yet that this observation only applies when the full quantity of water is employed in the Nitro-Sulphuric Acid. For as before shown, the setting power is injured by a weak Nitric Acid, but not so much by a stronger acid: hence No. 5 would produce a Collodion with sufficient power of setting if the amount of water in the Nitric Acid were reduced; but in this case the film would possess the objectionable properties of Pyroxyline made in strong acids, being glutinous and difficult to pour.

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* If any one should desire to examine the above acids as regards their strength or power of imparting NO_4 to the fibre of Cotton, let it be borne in mind that in the case of No. 1 the percentage amount of NO_4 in the Pyroxyline will increase considerably if the Cotton be permitted to remain for several hours in the cold acid. The proportion of Nitric Acid in this mixture is so small, being little more than one-fifth of the total bulk, that the Nitric Acid is in a measure *exhausted* in acting upon the fibre, and consequently a rather low substitution body is formed: the Cotton imbibes the liquid like a sponge, and for the first half-hour only those portions of the acid which touch the fibre produce any effect; afterwards, however, a process of diffusion goes on in the liquid, and fresh acid coming into contact with the fibre, more Peroxide of Nitrogen is communicated to it.

Effect of Raising the Temperature.—Although we have spoken of fluidity of Collodion, and tenacity of the film as affected by the relative proportions of water, Sulphuric Acid, and Nitric Acid present in the Nitro-Sulphuric Acid, yet such remarks must be taken very much in connection with the temperature at the time of putting in the Cotton, since the physical modifications produced by the two constituent acids are seen in an exaggerated degree when the Nitro-Sulphuric mixture is *heated.* An acid which gives an insoluble and explosive product in the cold, will yield Pyroxyline perfectly soluble at a higher temperature. Pyroxyline prepared in acids barely warm, makes Collodion which is glutinous and difficult to pour on large glasses, even although containing as little as two or three grains of the soluble Cotton to the ounce. The film soon becomes surface-dry, and repels the developer so that it cannot be made to flow up to the edge: on examination after fixing, it shows cellular spaces and structural lines. *Hot acids,* on the other hand, yield Pyroxyline of the kind which is easily soluble in Ether and Alcohol to the extent of eight or ten grains to the ounce of solvents, and the resulting Collodion is limpid and adherent to the glass. There is also an absence of structural marking in this Collodion, the transparent layer being nearly homogeneous, even when highly magnified.

The reader will perceive that the above physical effects of increased temperature are almost identical with those before attributed to a dilution of the Nitro-Sulphuric Acid with water. This is quite natural, because heat and dilution co-operate in increasing the action of the acids upon the fibre. What we have to do in preparing a Pyroxyline for fluid and adhesive Collodion, is to hit the exact point at which disintegration of the fibre commences, and to add more water, and raise the temperature a few degrees, if after an immersion of five or ten minutes the Pyroxyline appears strong and unyielding, like ordinary cotton.

Different forms of Cellulose.—Cotton, Straw, Pith, Flax, etc., with the manufactured fabrics produced from the same, may be converted into soluble Pyroxyline, but the product will be more or less different in each case. When a rather concentrated Nitro-Sulphuric Acid is used, Cotton may give a glutinous Collodion, and Calico a fluid Collodion. In another acid, weaker than the last, the Cotton succeeds well, whilst Calico instantly dissolves. The difference in the two cases appears to depend principally upon the *thickness of the fibre;* Calico produces Pyroxyline of the fluid kind, and is partially dissolved, because the Nitric Acid in acting on the outside portions of the closely-twisted fibre, is reduced in strength, and hence the interior of the fibre is left more nearly in the condition of Xyloidine. It is possible also, that with this weakening of the acid there may be a corresponding rise of temperature, which would assist in producing a powdery Pyroxyline, or in causing solution.

Linen, even when selected of the same thickness, yields a more limpid Collodion than Calico, and one of which the film is less tenacious and contractile. These peculiarities cannot be satisfactorily explained, unless they depend upon a difference in *composition;* which is not improbable, since it is known that Flax can be distinguished from Cotton by chemical tests, being more easily discoloured by the action of alkalies.

Both Linen and Calico undergo a change by constant use, which is recognized on making the material into Pyroxyline. Old and rotten rags are quickly disintegrated by the acid mixture, and the Pyroxyline produces a highly structureless Collodion, which adheres with much tenacity to the glass. *Paper* has been at different times much recommended for the preparation of Pyroxyline, but it will easily be gathered from the above remarks that it is an unfit material; for not only do different samples of paper vary greatly in thickness, which, as before shown, would affect the action of the Nitric Acid, but, being made both from Cotton and Linen rags, some of which rags are new and others old and rotten, they cannot be expected to produce uniformity. The Swedish filtering paper imported into this country for chemical purposes, has been stated to be uniform, but the Writer does not find the assertion correct; the Pyroxyline being at one time structureless and at another comparatively glutinous, even with the same Acids.

In addition to the materials mentioned above, others have been tried, such as China Grass, the Pith of the Jerusalem Artichoke, the Fibre of the Aloe, etc., but the result was only to confirm the opinion above expressed, that on each material the Sulphuric Acid, and also the Nitric Acid produces a different effect. The Fibre of the Grasses, including Flax, appears to be more easily disintegrated and dissolved both by Acids and Alkalies than that of Cotton, and to be convertible into sugar with greater facility.

A point of some importance, as regards the manufacture of Pyroxyline, is the cleansing of the Fibre thoroughly from adhering resinous matter, which, if allowed to remain, deoxidizes a portion of the Nitric Acid, and so far weakens it as to ensure the immediate destruction of a portion of the cellulose at high temperatures. A convenient substance to employ in cleansing is a diluted alkali, which converts the resin into a soap more or less soluble in water. It is probable that the differences which have been said to exist between Cotton of various growths may depend in part upon the presence or absence of this resinous matter. The Manufacturer who wishes to work with great accuracy, and to employ the largest quantity of water possible in the Nitro-Sulphuric Acid, should also bear in mind that Cotton is a hygroscopic substance and requires to be artificially dried. A minute proportion of moisture present upon the very surface of the Cotton, would produce a greater effect in causing solution than the same quantity of water added to the Nitro-Sulphuric Acid, since it would dilute only that portion of the Acid which touches the Fibre, and thus would cause a rise in the temperature.

Photographic Properties of Various Kinds of Pyroxyline.—In preparing Pyroxyline from the five different mixtures given in the table of composition of Nitro-Sulphuric Acid at page 109, it is found to differ in its Photographic properties as well as in its physical properties. As regards intensity of the Negative image, we observe that Pyroxyline made in the mixtures at the top of the scale, which contain an excess of the diluted Oil of Vitriol, tends to produce more intense images than Pyroxyline from No. 4 or No. 5, in which the diluted Nitric Acid is in excess. The difference in the two cases is caused by the Oil of Vitriol, since the same effect of increasing intensity can be obtained by parchmentizing the Fibre first and converting it into Pyroxyline afterwards: and it is not improbable that this action of the Sulphuric Acid in increasing intensity depends upon a conversion of the Cellulose into a substance resembling dextrine in its photographic action.

Irrespective of the proportions of the two Acids, the quantity of water in any mixture of Nitro-Sulphuric Acid will affect the photographic intensity of the resulting Pyroxyline and Collodion. This effect is evidently due to the same action of weak Nitric Acid as that which causes it to disintegrate the Fibre, for if we take a sample of Pyroxyline previously parchmentized by Oil of Vitriol, and capable of yielding great intensity in Collodion, we may destroy its properties in that respect most completely by dipping it for an instant in a warm mixture containing an excess of very weak Nitric Acid. When speaking of the Negative Nitrate Bath it will be shown that it loses its power of producing a dense picture if a little organic matter oxidized by Nitric Acid be added to it: it appears therefore that Nitric Acid is capable of producing with organic bodies a substance of unknown composition, which is injurious to the intensity of the photographic image. This subject however is not at present clearly understood, and we must therefore be satisfied with indicating the facts as they stand.

The *temperature* of the Nitro-Sulphuric Acid at the time of immersing the Cotton invariably affects the photographic properties of Pyroxyline. At high temperatures a portion of the Fibre is converted into a substance which has a bitter taste, and turns brown when treated with Alkalies. This substance is believed to be Nitro-Glucose, formed by the action of strong Nitric Acid upon Grape Sugar: the Grape Sugar itself being produced from the Cellulose by contact with the warm and diluted Sulphuric Acid. In studying the effect which this bitter product of decomposition is likely to produce, we may prepare Nitro-Glucose and add it to Collodion. Nitro-Glucose diminishes the sensitiveness of the film to obscure radiations, but increases the rapidity and intensity of the development in Negative pictures. Vigorous images are produced even in a very dull light, but they are always liable to be black and white without middle tints, or to solarize and become extremely red in the most exposed parts of the film, where the light acts strongly. Collodion made at very high temperatures, although possessed of great fluidity, adhesiveness, and freedom from structural lines, with other physical advantages before enumerated, is found less useful for ordinary work than samples prepared at a lower temperature and which are not so good in physical properties, being somewhat ropy in hot weather, and drying up more quickly after sensitizing. A film of this latter kind is very sensitive, and every radiation makes a distinct impression even after the shortest exposure.

The author of this Work is inclined to attribute the peculiarities of Collodion made from Linen, or from Paper manufactured out of partially decomposed rags, to the presence of Nitro-Glucose in the Pyroxyline. He has found that unless the temperature of the Nitro-Sulphuric Acid be kept low, there is a peculiar disposition to form the bitter resin, not only in Linen Fibre, and partially decayed Cotton Fibre, but also in the pure Cotton Fibre previously converted into vegetable parchment by the action of diluted Sulphuric Acid. In each case the Collodion is highly intense, and when shaken up with Carbonate of Potash assumes an amber-yellow colour, whereas a Pyroxyline nearly free from the bitter matter remains colourless for a time on treating the Collodion with Carbonate of Potash.

It may be proper before leaving this part of our subject to say a few words on an action which *Chlorine* appears to exert in the manufacture of Pyroxyline. The yellow Nitric Acid of commerce invariably contains a portion of Chlorine, and this is found to exert a decomposing action upon the Fibre, the result of which is to increase the fluidity of the resulting Collodion and also its intensity, but somewhat to diminish its sensitiveness. It is advisable therefore to employ a Nitric Acid from which the Chlorine has been eliminated, since any amount of intensity of Collodion may be obtained by sufficiently increasing the proportion of diluted Oil of Vitriol in the Nitro-Sulphuric Acid, or by raising the temperature, and avoiding the use of too much water in the acids.

In examining commercial samples of Pyroxyline prepared from Cotton-wool, the Writer has met with a variety which gives great intensity of Collodion with an average amount of fluidity. A quality of Pyroxyline similar to this may be prepared in a mixture of Nitro-Sulphuric Acid containing about two measures of Oil of Vitriol to one measure of Nitric Acid of ·145 (contaminated with a little Chlorine), and a quantity of water decidedly *less* than that given in the table at page 109. The temperature of the acid mixture must be sufficiently raised to disintegrate the fibre, and so to produce a Pyroxyline which occupies a small space when dry, has rather a yellow aspect, and is inclined to be dusty. The film from the resulting Collodion is not very sensitive, since it contains a notable portion of the bitter resin, but it answers remarkably well for a negative Collodion prepared with a mixed Iodide and Bromide, and its manufacture requires less nicety than the formula which the Author adopts, since the quantity of water in the acids is not so large.

Spontaneous Decomposition in Pyroxyline.—The Author has occasionally failed when using samples of Pyroxyline which have been kept for many months after preparation. A partial liberation of Oxides of Nitrogen appears to take place in some instances, forming an atmosphere of red fumes within the bottle. Pyroxyline which has undergone much decomposition from the use of a very high temperature in the process of manufacture may be expected to change in this way, and especially so if the acids are not thoroughly removed by washing; a little Sulphuric Acid left in the Pyroxyline would keep it continually damp, and perfect dryness is essential to the stability of Pyroxyline. From phenomena observed in the decomposition of Nitro-Glucose it is probable that constant exposure to light favours the change. The products of the spontaneous decomposition of Gun Cotton have been stated to be Oxalic Acid and a neutral organic substance having the composition of Gum.*

THE PLAIN COLLODION.

The relative proportions of Ether and Alcohol in Collodion affect both the physical and Photographic properties of the solution. This subject has been already alluded to at p. 103, but there are some additional observations to be made.

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* For some further properties of Pyroxyline not mentioned in this Section, see the Vocabulary, Part III.

The use of an excess of Alcohol is advantageous in preventing the Ether from evaporating quickly in hot weather. At temperatures of 90° and 100° Fahr. it is almost impossible, with Collodion containing but little Alcohol, to coat a large glass and immerse it in the Bath before the upper part becomes dry; consequently an uneven coating of Iodide is produced, with a blueness at the top edge. This happens especially when the Spirits are very strong and almost free from water. Another advantage of making Collodion with a large quantity of Alcohol is, that it more readily amalgamates with the Bath solution, and does not throw the liquid into greasy lines upon the surface of the film. There is however a practical limit to the use of Alcohol, inasmuch as not being a complete solvent of Pyroxyline it alters the structure of the film, rendering it gelatinous.

The quality of the Pyroxyline is the first important point to be considered in determining the relative proportions of Ether and Alcohol. With a sample of Pyroxyline made at a low temperature and in rather strong Nitro-Sulphuric Acid containing a minimum of Sulphuric Acid, barely enough Alcohol should be used in the *plain* Collodion to confer the requisite solubility, viz. an eighth or a twelfth part, by bulk, of the Ether: otherwise the iodized* Collodion will be very tender and easily torn, glutinous and difficult to pour, loosely adherent to the glass, and full of crapy lines and structural markings.

Pyroxyline prepared from Cotton-wool by the formula with a large excess of Oil of Vitriol will bear more Alcohol than the last, and with some advantage, for the contractility which makes it separate from the edges of the glass is lessened by the addition of Alcohol. The tendency to set quickly and produce water-markings at the upper edge of the plate is also to a great extent obviated, as is also the rapid surface-drying of the film after taking it from the Bath, which causes it to repel the developer, as before shown. The film, being nearly structureless and very tough, will bear a quantity of Spirit which in other cases would produce crapy lines and tenderness. If the Pyroxyline of this formula be made in acids containing the largest possible quantity of water, the proportion of Alcohol in the plain Collodion may be one-half of the Ether, which will give, after iodizing, equal bulks of the two Solvents; but if the Nitro-Sulphuric Acid was made with less water, then the proportion of Alcohol in the plain Collodion must not exceed *one-third* of the Ether, or the film will be woolly at the lower corner of the plate.

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* This observation supposes the plain Collodion and the iodizing compound to be kept in separate solutions; two measures of the latter being added to six measures of the former.

It will be found that the solubility of this tough kind of Pyroxyline is *increased* by employing the maximum quantity of Alcohol, so that if the plain Collodion be diluted with Ether, a precipitate will take place. With other kinds of Pyroxyline differently prepared, the addition of Ether to the plain Collodion produces no precipitate.

In the case of Pyroxyline prepared in Nitro-Sulphuric Acid containing equal bulks of Oil of Vitriol and Nitric Acid, with the maximum of water, it is advisable to reduce the quantity of Alcohol somewhat; for if too much Alcohol be employed, the *setting* of the Pyroxyline will be so greatly retarded that the upper edge of the film will become dry before the lower part has solidified sufficiently to take the Bath without precipitation of the Pyroxyline. Such an effect could not happen in the case of the first formula of page 109, containing Oil of Vitriol in excess, because it would be impossible to use such a mixture in a state sufficiently weak to destroy the property of setting in the resulting Pyroxyline: before that point was reached the cotton would dissolve in the acid.

The exact *strength* of the Alcohol used in Photography must always be noted, since the effect of water when present in any quantity is to produce viscidity of Collodion, and more rapid decomposition under the influence of the iodizing compound. The experience of Photographers is favourable to the employment of even a stronger spirit than that usually recommended; and when it can be obtained, the Alcohol of ·805 at 60° Fahr., sold in commerce as absolute, may be preferred, as a rule.

With the most horny kind of Pyroxyline, however, prepared by the first formula at page 109, a little water appears necessary, to open out the structure of the film and prevent it from assuming a condition in which it resembles Gutta Percha in being impervious to liquids; but in the case of Pyroxyline from formula No. 3, of page 109, such as is recommended for Positives, the film will be sufficiently porous, even with the whole of the Alcohol in the absolute state. With formula No. 1 the Alcohol of ·805 may also be employed, if the proportion be increased until it nearly doubles that of the Ether.

Photographic Effect of Excess of Alcohol in Collodion.—The addition of Alcohol to Collodion lessens the contractility of the film, and renders it soft and gelatinous. This condition is favourable to sensitiveness, perhaps from the play of affinities being promoted by the loose manner in which the particles of Iodide are held together. The extra sensitiveness obtained by use of Alcohol however does not increase after a certain point: on the contrary, it diminishes, for it appears to be necessary to extreme sensitiveness that the film should coagulate within a certain time after it has been coated, and therefore the addition of Alcohol must be stopped when the film loses its ready setting qualities, and is not coherent under the finger. Hence a porous Collodion is soon injured in sensitiveness on adding too much Alcohol, but a strong and tough Pyroxyline will bear equal bulks of the two Solvents without loss in that respect.

The above observation as to the effect of excess of Alcohol in diminishing the sensitiveness of the film to dark objects applies particularly when the atmosphere is cold and damp, and evaporation is retarded. At a very high temperature and in a dry air, it does not apply, since the presence of Alcohol is then useful in preventing the film from becoming surface-dry, especially when it is necessary to keep the sensitive plate for a long time between exposure and development.

Intensity of Negative is much favoured by using a full quantity of Alcohol,* and particularly when large glasses are coated, and long focus lenses, which work slowly, are employed. The difference is doubtless due in part to the structure of the film being opened out by the Alcohol, so as to assist the developer in penetrating, and partly to the rapidity of evaporation and consequent surface-drying being diminished. Hence in hot weather the Alcohol acts very beneficially, and with Collodion made almost entirely of Ether, the Negatives are unusually weak at such times. Pyroxyline of the horny kind is especially liable to lose intensity at high temperature unless the Alcohol be added freely so as to prevent the film from becoming hard and impervious.

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* For full particulars as to the purity of Alcohol for Photographic purposes see the Vocabulary, Part III.

Decomposition of Plain Collodion by Keeping.—Plain Collodion tends to become more limpid by keeping, and often acquires the property of eliminating Iodine rapidly from the iodizer; but the rapidity with which the change takes place, varies much with the mode of preparing the Pyroxyline and with the quality of the Ether. Supposing all the materials to be pure, the decomposition after keeping for several months in a cool and dark place is very slight, and is generally considered to improve the quality of the Negative rather than otherwise: it imparts a slightly red or purple tone to the image, without much affecting the sensitiveness, and hence many prefer to keep a stock of Collodion always on hand, that it may settle down clear, and "ripen." This proceeding however would be very far from safe with an unstable Pyroxyline, or an inferior Ether, since the Oxides of Nitrogen would then be set free from the Gun Cotton, and injury to the sensitiveness would result from elimination of Iodine after iodizing.

When great stability is an object, as in exporting Collodion to foreign climates, the Pyroxyline ought not to be made in such a way as to produce much *decomposition* in the Nitro-Sulphuric Acid. For instance, if we take pieces of old linen and immerse them at a temperature of 150° Fahrenheit in a Nitro-Sulphuric Acid made purposely very weak, the greater part will dissolve, but a few fragments remain, which, when washed and applied to the tongue, have a bitter taste. In this case the Pyroxyline is partially decomposed in the Acid, and Collodion made from the product might work well at first, but after keeping for twelve months in the plain state would probably be as thin as water, and produce a rotten and insensitive film.

The best kind of Pyroxyline for yielding a stable Collodion, according to the Author's experience, is that made from Cotton-wool, and at rather a low temperature. This preparation has been proved to retain its original properties *nearly* unchanged for nine months. The test for decomposition of Pyroxyline is *agitation of the Collodion with dry Carbonate of Potash.* When so treated it should remain colourless for a certain time: if it assume a brown tint in less than two hours, traces of the compound above named as resembling Nitro-Glucose are present.

Plain Collodion, made at a temperature of 170° to 180° Fahr., will keep well for a few weeks, but when exported to a distant climate, and subjected to an elevated temperature, liberates Iodine from Iodide of Potassium somewhat quickly, and is useful only for taking Positives, or Negative views when exposure is not an object. Carbonate of Potash shaken up with this kind of Collodion strikes a brown colour.

A point which should not be overlooked in preparing Collodion for keeping, is the length of time during which the fibre of the Cellulose remains in the Nitro-Sulphuric Acid. A short immersion (five minutes) is the best, and if the material be left for half an hour or longer, as may sometimes be done without solution taking place, the Collodion will often acquire by degrees the property of striking a brown colour with Iodide of Potassium.

The quality of the *Ether* is very important in making a Collodion of uniform properties. It is possible to obtain an Ether which will remain for months without assuming the condition known as "ozonized," in which it liberates Iodine from Iodide of Potassium; but Ether containing Aldehyde or organic impurity will soon change.

The Photographer will be guided partly by the quality of his Ether in deciding as to the best formula for a Pyroxyline, because an inferior Ether soon renders the Collodion rather limpid through formation of Acetic Ether or some similar product, by which the setting power of the Pyroxyline is diminished. It must also be borne in mind that when this impure Ether liberates Iodine in the iodized Collodion, a corresponding portion of the alkali Potash is set free, which, as we shall presently show, adds to the limpidity and lessens the setting powers. To meet this difficulty the Pyroxyline should be made slightly more tough and contractile than is necessary, which may be effected by reducing the temperature of the Acid a few degrees. Also, since impure Ether soon becomes ozonized, a high temperature of Nitro-Sulphuric Acid ought to be avoided, as likely to render the Pyroxyline unstable.

Inferior Ether usually produces a more intense Collodion than pure Ether, but the plain Collodion does not keep for any length of time without change, soon losing its sensitiveness, and yielding pictures which are black and white without middle tints. A rapid elimination of Iodine takes place on adding the iodizer, and the film is weak and rotten. In some cases commercial Ether is contaminated with organic Oils having a foul smell, or contains traces of the Alkali employed in the processes of purification. The latter impurity is particularly objectionable, because Alkalies and Carbonated Alkalies decompose Collodion, rendering it limpid and destroying the setting properties. "Methylated Ether" (see the Vocabulary, Part III.) is largely employed in the manufacture of Collodion, but where expense is not an object, the Writer recommends the pure Ether in preference. (Read the article "Ether," in the Vocabulary, for further particulars.)

IODIZING SOLUTIONS.

Different Iodides vary in their effect upon plain Collodion. Those which have an acid reaction, like the Iodide of Cadmium, may be expected to increase the glutinosity. But Alkaline Iodides, such as Iodide of Potassium or Ammonium, render it limpid and structureless. Fixed Alkalies or Alkaline Carbonates have a more marked effect than Alkaline Iodides, as may be shown by agitating plain Collodion with powdered Carbonate of Potash: in the course of a few days it becomes as fluid as water. The first effect of the Alkali however upon Pyroxyline made by the formula with excess of Oil of Vitriol is to render the Collodion *glairy*, so that the bottle may often be completely inverted without any immediate loss. The same observation applies to Alkaline Iodides: they thicken the Collodion slightly in the first instance, and afterwards render it more limpid. When Collodion gradually becomes limpid under the action of an Alkaline Iodide, it loses its power of setting upon the glass; but there is a remarkable difference between Collodions in the rapidity of this change, and those which are tough and unyielding when newly made withstand the action of the Alkali for a much longer time.

The reader will perceive that the effects now attributed to the action of alkaline Iodides upon Collodion, viz. limpidity, and a diminished power of setting, are the same as those spoken of under the head of dilution of the Nitro-Sulphuric Acid with water. There is however this important difference in the two cases, that in the former an increase of photographic intensity accompanies the porosity, but in the latter the intensity is diminished, as already shown at page 114.

Iodide of Cadmium.—The stability of this compound is its great recommendation: Ether, unless highly ozonized, has little or no effect in liberating Iodine from it. Another advantage of the Iodide of Cadmium is that it does not destroy the setting properties of the pyroxyline as the alkaline Iodides eventually do.

The Collodion should be prepared purposely when Iodide of Cadmium is used as an iodizer. Collodion containing Pyroxyline made at a low temperature and in rather strong acids, works tolerably well after iodizing with the Potassium or Ammonium compound and keeping until liberation of Iodine and liquefaction have taken place; but with Iodide of Cadmium it would be in every respect unsatisfactory, flowing in a slimy manner upon the plate, exhibiting crapy lines, repelling the developer, and splitting away from the glass on drying. When the Pyroxyline is made in strong acids at a very high temperature, the Collodion is often sufficiently fluid, but yet is not altogether adapted for iodizing with the Cadmium Salt, from its tendency to produce "woolliness" or unevenness of film at the lower edge of the plate. The proper kind is that prepared in weak acids, and sufficiently parchmentized by the Oil of Vitriol to give the requisite degree of intensity.

Iodide of Potassium.—This Salt is well adapted for iodizing Collodion not required to possess keeping properties, but its sparing solubility in Alcohol and Ether is an objection. Collodion containing 4½ parts of Ether of ·725 to 3½ of Alcohol ·816, will carry nearly three grains of Iodide of Potassium to the ounce. With equal bulks of Ether and Alcohol the full quantity, viz. four grains, may be dissolved. Five parts of Ether with three of Alcohol will not take more than 2 or 2½ grains to the ounce. The admixture of Iodide of Cadmium with Iodide of Potassium increases the solubility of the latter Salt, by forming a double Salt, the Iodide of Potassium and Cadmium. To produce this compound, which is well fitted for iodizing Collodion containing five parts Ether to three of Alcohol of ·816, equal weights of the two Iodides may be taken. These proportions are not strictly correct, but they are sufficiently near for practical purposes.

It may also be remarked that the quantity of an alkaline Iodide which any Collodion will carry depends partly upon the Pyroxyline. With that particular kind of Pyroxyline which is recommended for Negatives in this Work, no more than 3½ grains per ounce must be employed, otherwise the Iodide of Silver will appear to burst out upon the surface of the film at the lower edge, and marks will result. By mixing the Iodide of Potassium with Iodide of Cadmium, or by using Iodide of Cadmium alone, a larger quantity of Iodide may be used without the appearance of markings.

The effect of using an iodizing solution containing more Iodide of Potassium than the Collodion will retain in solution, is not always to produce an immediate precipitation, such as would result if the Pyroxyline were omitted and the iodizing solution added to an equivalent quantity of Ether and Alcohol. The presence of the Pyroxyline prevents a visible deposition, but the Collodion will produce a spotted image, and after standing for some days crystals will form upon the sides of the bottle.

When the whole of the Alcohol contained in the Collodion is of the strength of ·805, commercially known as "absolute," it will scarcely be safe to iodize with Iodide of Potassium only, unless the proportion of Alcohol is nearly double that of the Ether much however will depend upon the degree of dryness of [illegible] Ether itself, since the commercial Ether often contains [illegible] dissolved in it, in sufficient quantity to prevent the precipita[illegible] of the Iodide of Potassium. The preparation of an iodizing [illegible] tion of Iodide of Potassium is a troublesome process with [illegible] of ·805, since it is necessary to pulverize the Iodide very [illegible] and to boil the spirit upon it; in cold weather such [illegible] is apt to deposit cubical crystals upon the sides [illegible] containing it.

Commercial Iodide of Potassium is often cont[illegible] Carbonate of Potash. This Salt has an injurious [illegible] in throwing a white deposit of Carbonate of Cad[illegible] mixed Iodides are used, but also in reacting upo[illegible] and producing rapid liquefaction, as before show[illegible] of Potassium is now prepared purposely for Ph[illegible] crystals have a slightly yellow tint, and the A[illegible] liberates Iodine slowly on exposure to Light.

Iodide of Ammonium is useful in iodizing C[illegible] is required to add also a portion of Bromide; [illegible] *Potassium* were [illegible] in such a case, a whit[illegible] form on [illegible] the sparing solubility of Br[illegible] [illegible] water. Collodion contai[illegible] [illegible] not carry mo[illegible] to the ounce, [illegible] dissolve a much larger quantity of Bromide of Ammonium or Bromide of Cadmium. The only objection to the use of Iodide of Ammonium is its instability, and the difficulty of invariably obtaining it in a pure state, the Writer having found that most of the samples prepared by aid of Sulphuretted Hydrogen or Hydrosulphate of Ammonia contain traces of a Sulphur compound, and are inferior to those made in the moist way, by precipitation. When Iodide of Ammonium becomes brown by keeping, it may be decolorized by shaking it up in a bottle with a little Ether, and drying upon blotting-paper.

Iodide of Sodium is intermediate in solubility between Iodide of Potassium and Iodide of Ammonium, and would be a valuable compound for iodizing if it could be obtained commercially in a pure state.

Iodide of Iron was formerly used in Photography, but has now become obsolete. It produces a very sensitive Collodion at first, but soon reacts upon the Pyroxyline, and the Collodion becomes reduced to the condition of a jelly. The Nitrate Bath is also thrown out of order, Protonitrate of Iron being formed, which changes to Pernitrate and precipitates Metallic Silver on the sides of the trough.

Chemical and Photographic action of the various Iodides in Collodion.—With recently iodized Collodion the difference in sensitiveness between the various Iodides is not very marked if they are in a pure state. The presence of Carbonate of Potash, Iodate of Potash, or Chloride of Potassium in the commercial Iodide of Potassium at once diminishes the sensitiveness; and any trace of a Sulphur compound in the Iodide of Ammonium will have the same effect.

The *intensity* of Negative Collodion does not vary materially with the Iodide, if the Collodion be tested soon after iodizing. Nevertheless by close observation minute differences can be detected, and Iodide of Potassium will be found to give a somewhat more vigorous picture than Iodide of Ammonium. With any Iodide also the intensity will be lessened by adding too large a quantity of the Iodide, and especially when the setting power of the Collodion is small, for it must be remembered that Pyroxyline has always more or less of an organic reaction towards the Salts of Silver, and therefore the Iodide of Silver ought to be brought into close relationship with it. If from any cause, such as excess of Iodide, deficiency of setting power in the Collodion, etc., the sensitive film of Iodide be allowed to lie loosely upon the surface of the Collodion, the picture will be very feeble, and will often fall away when the fixing agent is applied.

After Collodion has been kept for a time in the iodized state, both the sensitiveness and the intensity will vary with the Iodide chosen, because, as before shown, an affinity exists between the Pyroxyline and the base of the Iodide. Alkaline Iodides are soon decomposed by Collodion, and hence a loss of sensitiveness, depending partly upon the retarding effect of free Iodine, and partly upon the new compound formed by the liberated Alkali. The liquefaction of the Collodion, and its diminished power of setting upon the glass, must also be supposed to be injurious to sensitiveness (p. 119). The *intensity* however will increase in consequence of these changes, since free Iodine, although it lessens intensity in a dull light, tends to prevent feebleness of the image from solarization in a strong light; and the compound formed by the trace of liberated Alkali, whatever be its nature, has a direct action in adding to the intensity. The liquefaction of the Collodion is also serviceable up to a certain point, by removing the impermeability to the developer which the more dense and horny kinds of Collodion exhibit.

Iodide of Cadmium is the most stable of all the Iodides, yet with Iodide of Cadmium as an iodizer, an amount of change sufficient to lessen the sensitiveness of the Collodion to very dark objects eventually takes place, and with an unstable Pyroxyline or impure Ether, this change may be evident even in a few weeks. Iodide of Cadmium also increases the intensity of Collodion after a long keeping, especially with Pyroxyline made in rather strong acids. In such a case the Collodion gradually becomes slightly gelatinous, the film solarizing strongly in the parts most acted on by the Light, and the image exhibiting a bright red colour when viewed by transmission. This state of Collodion is well fitted for photographing in a dull light.

The nature of the Pyroxyline must also be taken into account in estimating the probable effect of iodizing with an Alkaline Iodide. If it has undergone decomposition in the manufacture, the sensitiveness of the Collodion will soon be lost; but if prepared at low temperatures it remains for a longer time unchanged: of all kinds of Pyroxyline the least stable after iodizing is that prepared from Linen, in weak acids, and at a high temperature.

A point which affects the keeping qualities of a Collodion, or its stability after iodizing, is the presence of *Bromide* combined with the Iodide. Collodion so made assumes the usual yellow tint when mixed with the iodizing solution; but in the course of some hours either the whole or a part of the free Iodine appears to be re-absorbed. This change takes place most rapidly in the case of methylated Ether, but it may be seen more or less even with pure Ether and pure Alcohol. No satisfactory explanation can be given.

To facilitate the comprehension of the decompositions which take place in iodized Collodion, let the following experiments be made. Take Nitro-Glucose and add it in small quantity to ordinary Collodion iodized with the Potassium compound: the elimination of Iodine will be somewhat more rapid than usual, the Collodion at the same time losing sensitiveness and gaining intensity. Next dissolve Nitro-Glucose in Spirits of Wine, and boil it in a test-tube with powdered Carbonate of Potash: the liquid becomes brown, and evolves a smell of burnt sugar; a few drops of it in iodized Collodion rapidly destroy the sensitiveness, but add much to the blackness of the Negative. In a third experiment introduce a portion of a reducing agent, such as grape-sugar, into iodized Collodion: the result will be to lessen the sensitiveness on keeping, and to increase the intensity. The experiment last described shows that not only the nature of the particular Iodide, and that of the Pyroxyline, but also the presence of foreign organic substances may affect the keeping properties of iodized Collodion; hence the importance of using Ether which has been carefully freed from traces of Aldehyde, etc., since even the employment of an Iodide as stable as that of Cadmium will not prevent decomposition if substances are present in the Collodion which have an affinity for Oxygen.

Another experiment, illustrating the effect of changes in Collodion after iodizing, is the following:—Take Nitrite of Soda, and boil with it Alcohol of ·805 until a saturated solution has been obtained: a few minims of the liquid added to an ounce of iodized Collodion, will increase the intensity. A Nitrite is one of the products of decomposition of Collodion by alkalies, or alkaline Iodides, and may sometimes be seen in the form of well defined crystals at the bottom of the bottle.

MODE OF TESTING COLLODION CHEMICALLY.

So much having been said of the mechanical and chemical differences in various samples of Pyroxyline and Collodion, it may be well to give a few simple rules for testing these substances. First, boil a small portion of the Pyroxyline in a test-tube with glacial Acetic Acid: if it remains unacted on, the proportion of Peroxide of Nitrogen in it is greater than the author advises, but if it becomes gummy and transparent, it will be likely to yield an adhesive Collodion. This test often fails, from the commercial glacial Acetic Acid being diluted with water, in which case it is no longer a solvent for Pyroxyline. Boil a second portion of the Pyroxyline with Alcohol of sp. gr. ·805, sold as absolute: it ought to dissolve partially, but the presence of 4 per cent. of water in the spirit will prevent the solution.

Third, dissolve six grains of the Pyroxyline in half an ounce of Ether of ·725 mixed with half an ounce of Alcohol of ·815 containing 3½ grains of Iodide of Potassium; a flocculent deposit of undissolved matter will generally indicate that very weak acids were used in making the Pyroxyline. Now take a clean glass plate and pour a little of the Collodion upon it. If it runs with difficulty, soon gelatinizes, and can be pushed aside in a skin, the proportion of Sulphuric Acid in the Nitro-Sulphuric Acid was not greater than twice that of the Nitric Acid: if the proportions had been as three to one, the film would have allowed the finger to pass over it without breaking, when examined at this stage. The Collodion however may appear thus adherent to the glass, even with acids in the proportion of equal bulks, *when the acids are very weak;* but in the former case this effect will be seen quite independently of the quantity of water in the acids. Practically the test is useful, and the writer always begins by examining a new Collodion in that way: if he can push the film aside before dipping in the Bath, he concludes that the Pyroxyline was not sufficiently disintegrated to yield a fluid and adhesive Collodion. Pyroxyline made from linen or Swedish paper, will generally prove satisfactory as far as this test is concerned. Collodion made from methylated spirits, which failed with the test at first, will often satisfy it after a few months keeping in the plain state (p. 121).

Having examined the Collodion in the way above described, divide what remains into two parts, and agitate one half with dry Carbonate of Potash; the rapidity with which it turns yellow will be a guide to its probable photographic intensity, and to its stability after iodizing. Experience is required in employing this test, but a practical operator will find it useful in deciding whether the Pyroxyline was made at a temperature sufficiently high to generate Nitro-Glucose. The Ether contained in the Collodion for this experiment must be pure, since inferior samples of Ether may become yellow with a Carbonated Alkali even when not containing Pyroxyline.

The second half of the Collodion iodized with the Iodide of Potassium should be put aside in a dark cupboard, that the rapidity with which the Iodine is eliminated may be observed. The varieties of Pyroxyline which decompose Iodide of Potassium very readily, are those which have been strongly parchmentized by the use of the formula containing three volumes of Oil of Vitriol to one of Nitric Acid, and the higher the temperature of the Nitrosulphuric Acid the more rapid the change. Pyroxyline from old linen or paper is more unstable than that last described, and if it has been allowed to undergo any spontaneous decomposition by want of proper care in keeping, it is still worse. Traces of Sulphuric Acid left in the Pyroxyline from improper washing, will have the same effect of discolouring the iodizer; but in this case the plain Collodion ought to redden blue Litmus in twelve hours. Observe that this test may fail completely when the Ether and Alcohol are not genuine, since the commercial spirits often reabsorb the Iodine and thus give a delusive appearance of purity.

One more test may be mentioned. To ascertain whether a sample of Pyroxyline has been strongly parchmentized by the Oil of Vitriol in the process of manufacture, dissolve four grains in one drachm of Alcohol of ·805 mixed with two drachms of Ether of ·720. If the formula of three of Sulphuric Acid to one of Nitric Acid was adopted, the plain Collodion ought to become milky on diluting with pure Ether. The presence of a little water in the Ether, or the use of too dilute an Alcohol, interferes with the test, since the precipitated flocculi are soluble in water.

SECTION II.

The Chemistry of the Nitrate Bath.

The solution of Nitrate of Silver in which the plate coated with Iodized Collodion is dipped, to form the layer of Iodide of Silver, is known technically as *the Nitrate Bath.* The Chemistry of Nitrate of Silver has been explained at page 12, but there are some points relating to the properties of its aqueous solution which require a further notice.

Solubility of Iodide of Silver in the Nitrate Bath.—Aqueous solution of Nitrate of Silver may be mentioned in the list of solvents of Iodide of Silver. The proportion dissolved is in all cases small, but it increases with the *strength* of the solution. If no attention were paid to this point, and the precaution of previously saturating the Nitrate Bath with Iodide of Silver neglected, the film would be dissolved when left too long in the liquid.

This solvent power of Nitrate of Silver on the Iodide is well shown by taking the excited Collodion plate out of the Bath, and allowing it to dry spontaneously. The layer of Nitrate on the surface becoming concentrated by evaporation, eats away the film and produces a transparent, spotted appearance.

In the solution of Iodide of Silver by Nitrate of Silver a *double salt* is formed, which corresponds in properties to the double Iodide of Potassium and Silver in being *decomposed* by the addition of water. Consequently, in order to saturate a Bath with Iodide of Silver it is only necessary to dissolve the total weight of Nitrate of Silver in a small bulk of water, and to add to it a few grains of an Iodide; perfect solution takes place, and on subsequent dilution with the full amount of water, the excess of Iodide of Silver is precipitated in the form of a milky deposit.

The above named double salt of Iodide of Silver and Nitrate of Silver has been termed by Schnauss the "Iodo-

Nitrate of Silver," and although in the Collodion Nitrate Bath it is present only in small quantities, and in a state of solution, it is quite possible to obtain it in well defined crystals. No corresponding compounds containing Bromide and Chloride of Silver, are known, and hence it will not be necessary to saturate the Bath with those salts when it is desired to use them in Collodion.

Although the addition of water to the Negative Bath, renders it milky by precipitation of Iodide of Silver, dilution with Alcohol has not the same effect. In the Chapter on dry Collodion it will be shown that Iodide of Silver combines with Nitrate of Silver in greater proportion and in a more permanent manner, when the Nitrate is previously mixed with organic matters.

Acid condition of Nitrate of Silver.—A solution of Nitrate of Silver prepared from the commercial Nitrate has usually an acid reaction; the crystals having been imperfectly drained from the acid mother-liquor in which they were formed. Hence, in making a new Bath it is advisable not only to saturate it with Iodide of Silver, but to neutralize the free Nitric Acid it contains.

The quantity of this Acid is very variable. If the Nitrate has been carefully dried at 240° Fahrenheit, and then crystallized a second time, no Nitric Acid can be detected, the concentrated aqueous solution slowly restoring the blue colour of reddened Litmus. This alkaline effect upon reddened Litmus the Writer believes to be the proper reaction of pure Nitrate of Silver, since he finds it to exist in samples of Nitrate which have never undergone fusion. On the other hand, Nitrate of Silver which has been crystallized only once from the acid mother-liquor, without any attempt at careful drying, is often so decidedly acid that it cannot be employed in Photography until neutralized.

The Nitrate Bath, although perfectly neutral when first prepared, may become acid by continued use, if Collodion containing much *free Iodine* be constantly employed. In that case a portion of Nitric Acid is liberated, thus:—

Nitrate of Silver + Iodine
= Iodide of Silver + Nitric Acid + Oxygen.*

If the Bath contains *Acetate* of Silver, free Iodine liberates Acetic Acid in place of Nitric Acid; and Nitric Acid added to such a Bath neutralizes itself and displaces Acetic Acid, thus:—

Nitric Acid + Acetate of Silver
= Nitrate of Silver + Acetic Acid.

The actual quantity of acid liberated by Collodion which has become brown from decomposition, is very inconsiderable, and it is a common error to be continually neutralizing the Nitrate Bath. When, however, the trough which holds the Bath is narrow, and the plates large, a minute addition of Alkali may occasionally be required, to prevent the film from losing sensitiveness, and yielding weak metallic Negatives.

Alkaline condition of the Bath.—By "alkalinity" of the Bath is meant a condition in which the blue tint is restored to reddened litmus-paper. This change, when rapid, indicates that an Oxide is present in solution, which by combining with the acid in the reddened paper neutralizes it and removes the red colour.

If a small portion of caustic Potash or Ammonia be added to a strong solution of Nitrate of Silver, it produces a brown precipitate, which is Oxide of Silver.

Ammonia + Nitrate of Silver
= Oxide of Silver + Nitrate of Ammonia.

The solution, however, from which the precipitate has separated, is not left in a neutral state, but possesses a distinct alkaline reaction, since Oxide of Silver is sparingly soluble in water, and the solution restores the blue colour of reddened Litmus. Both Oxide of Silver and Carbonate of Silver are [illegible] soluble in water containing Ni[illegible] salt is continually accumu- [illegible]mpounds of Ammonium are

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* [illegible] Iodate of Silver in the film, a retarding [illegible] quantity.

An alkaline Bath is fatal to success in Photography, producing that universal darkening of the film on applying the developer to which the name of "fogging" has been given. Hence care must be used in adding to the Bath substances which tend to make it alkaline. Collodion containing free Ammonia, often sold in the shops, gradually does so. The use of Potash, Carbonate of Soda, Chalk, or Marble, to remove free Nitric Acid from the Bath, has the same effect, when an excess is employed; and hence a trace of Acetic Acid must afterwards be added.

The mode of testing a bath for alkalinity is as follows:—a strip of porous blue litmus-paper is taken and held to the mouth of a bottle of glacial Acetic Acid until it becomes reddened; it is then placed in the liquid to be examined and left for ten minutes or a quarter of an hour. If Oxide of Silver be present in solution, the original blue colour of the paper will slowly but gradually be restored. This experiment must not be made in a strong light, or the litmus-paper will darken, and the blue colour be obscured. Indeed it is always somewhat difficult to examine a Nitrate Bath by test-papers, since the pure Nitrate of Silver has a slightly alkaline reaction; and hence the Photographic effect of alkalinity, viz. cloudiness of the image, will to the amateur, afford a more certain guide. The Writer believes that the use of *Ammonia* for the purpose of neutralizing the Bath is the most common cause of failure from alkalinity, few being aware that *a single drop of strong Ammonia* will neutralize a comparatively large quantity of acid.

Acetate of Silver in the Nitrate Bath.—In preparing a new Bath, if the crystals of Nitrate of Silver are acid, it i[illegible] add an alkali in small quantity. This removes [illegible] Acid, but leaves the solution faintly alkaline [illegible] of Silver. Acetic Acid is then dropped in, [illegible]mbining with the Oxide of Silver, forms Ace-[illegible]e.

[illegible] Silver is not formed by the simple addition of [illegible] to [illegible], because its production under such [illegible]ply the liberation of Nitric Acid;

but if an alkali be present to neutralize the Nitric Acid, then the double decomposition takes place, thus—

Acetate of Soda + Nitrate of Silver
= Acetate of Silver + Nitrate of Soda.

Acetate of Silver is a white flaky salt, sparingly soluble in water. It dissolves in the Bath only in small proportion, but yet sufficiently to affect the Photographic properties of the sensitive Collodion film. The observance of the following simple rules will obviate its production in injurious quantity:—First, when it is required to remove free Nitric Acid from a bath *not containing Acetic Acid* a solution of Potash or Carbonate of Soda may be dropped in freely; but the liquid must be filtered before adding any Acetic Acid, otherwise the brown deposit of Oxide of Silver will be taken up by the Acetic Acid, and the Bath will be charged with Acetate of Silver. Secondly, in dealing with a Bath containing both Nitric and Acetic Acid, employ an alkali *much diluted* (Liquor Ammoniæ with 10 parts of Water), and add a single drop at a time, coating and trying a plate between each addition; the Nitric Acid will neutralize itself before the Acetic, and with care there will be no formation of Acetate of Silver in quantity.

The question is sometimes asked, how Acetic Acid may be removed from the Nitrate Bath, and Nitric Acid substituted? This operation is somewhat difficult to effect. Nitric Acid, when present in excess, can be neutralized and converted into a *Nitrate*, which is nearly or quite inert in Photography; but to neutralize Acetic Acid is to form an *Acetate*, which is not inert; and the subsequent addition of Nitric Acid to such a solution again liberates Acetic Acid. Evaporation to dryness is the only means of effectually eliminating the Acetic Acid from the Bath, and to this proceeding there are grave practical objections, as will presently be shown.

Organic Matter in the Nitrate Bath.—Nitrate of Silver has an affinity for certain kinds of organic matter, and when such substances are present, the Photographic action of the Bath is in some way interfered with.

Commercial crystallized Nitrate of Silver is frequently contaminated with traces of an impurity, which is probably produced by organic matters falling into the Nitric Acid employed in dissolving the Silver. Repeated recrystallization is required to remove this substance. If allowed to remain, it injures the sensitiveness of the film to obscure radiations, makes the Negative weak and metallic, reverses the action of the light, and produces either fogging or markings of various kinds, the result of irregular reduction of Silver.

Solutions of Nitrate of Silver often acquire organic contamination by being kept in troughs of Gutta-percha. The Writer is of opinion that pure Gutta-percha has little action upon Nitrate of Silver, but that the commercial article is usually adulterated. Caoutchouc is also without action, but Caoutchouc vulcanized with Sulphur, such as is used for the tops of watertight baths, will decompose the Nitrate of Silver by degrees. Baths injured by impure Gutta-percha, produce fogging of the film, streaks of irregular development, and quick discoloration of the solution of Pyrogallic Acid, attended with variations in the density of the Negative picture: in the Appendix will be found a method of coating the sides of the Gutta-percha with shellac, to prevent this decomposition as far as possible.

The presence of one variety of organic matter in the bath, is indicated by excessive density of the Collodion picture, with red solarization in the most exposed parts, accompanied in some instances, but not invariably, with diminished sensitiveness to weak radiations. This state, which is the reverse of that described as resulting from organic matter oxidized by Nitric Acid, may happen in the case of Nitrate of Silver obtained by evaporating old baths to the crystallizing point, or it may occur after using Collodion containing Grape Sugar. Glycyrrhizine, or Liquorice Sugar, in Collodion, does not dissolve out into the bath so readily as Grape Sugar, but when Collodion containing Glycyrrhizine is employed constantly, the

Nitrate Bath eventually gives Negatives with a density greater or less than that obtained by use of pure Nitrate of Silver. Glycyrrhizine purposely added to the bath increases the intensity of the image in some states of Collodion, but the solution so treated is prone to change, and after some weeks' keeping the intensity of image may be materially lessened.

Albumen and Gelatine soon decompose Nitrate of Silver, and hence the dipping of a few dry albuminized plates, or the floating of chloride-papers intended for the printing process, upon a Collodion Bath, would effectually disorder it, and almost certainly give rise to fogging.

Alcohol and Ether react very slowly upon solution of Nitrate of Silver, and Pyroxyline is almost without effect. Hence when *pure* Collodion is employed, the bath may be kept for many months without much appreciable change. It should however be carefully excluded from light, or the sides of the bottle will be covered with a delicate layer of reduced Silver. Methylated Spirit of Wine is seldom sufficiently free from volatile oil to remain long in the bath without producing partial reduction.

Oil of Cloves counteracts in a measure the effect of Iodine in old coloured Collodion, and is a useful addition in some instances, but it will by degrees react upon the bath, and render it useless for a very delicate process. Slight fogging occurs which can only be removed by acidifying the solution with Acetic Acid. Gallic Acid has a still more marked effect upon the bath; it first gives increased sensitiveness of the Collodion film, with a tendency to fog, but afterwards produces a condition of bath in which the sensitiveness is much impaired, but the intensity of Negative is great, even when the pictures are taken in a feeble light, or after acidifying the bath with Nitric Acid.

Collodion containing common Rosin, has been recommended for use in the dry Collodion process; but the Rosin finds its way into the bath, and spoils it for the wet process, soon producing solarization of the most exposed parts of the plate, and altering the appearance of the film of Iodide, so that it becomes pale and blue, instead of being yellow and creamy.

The effect produced by organic matters in the bath will be more intelligible if we explain that not only Nitrate of Silver, but also *Iodide of Silver* has an affinity for a certain class of these bodies. Hence when a Collodion film is dipped in a bath of the kind described, a trace of organic matter is carried down and retained in the film. This applies especially to *Albumen,* which has so decided an affinity for Iodide of Silver, that its presence will entirely alter the colour of the film, and render it blue and transparent. A state of bath in which the Collodion film, instead of being yellow and creamy, appears blue or opalescent, may be produced by organic matter, as well as by a deficiency of Nitrate of Silver.

To remove organic matter from the bath, it has been recommended to expose it for two or three days to a bright sunlight; the greater part then separates in combination with reduced Oxide of Silver. This mode is unsatisfactory at the best, but it may sometimes be adopted as a last resource. Kaolin (see the Vocabulary), or freshly precipitated Oxide of Silver, will absorb and retain some kinds of organic matter, such for instance as Albumen, but in other cases will be without effect. An increase of sensitiveness to the extent of one-half, has in the Writer's experience been produced by shaking up an impure bath with Kaolin; so that this plan will often repay a trial.

Use of Fused Nitrate of Silver for the Bath.—Fusion has been resorted to with a view of expelling traces of Nitric Acid from the crystallized Nitrate of Silver, and thus lessening the trouble of preparing the bath. It must be observed however that decomposition of the Nitrate is liable to occur in melting, *if the crystals are not chemically pure.* A trace of any organic substance, such as a bit of cork, or a fragment of gelatine adhering to the sides of the porcelain dish, would at the melting point of Nitrate of Silver remove Oxygen, and produce *Nitrite of Silver:* a safer plan is therefore to pulverize the Nitrate and dry it in a hot-air bath, at about twenty degrees above the temperature of boiling water. Supposing the Nitrate to be absolutely free from organic matter, there would be no danger of forming Nitrite in the process of fusion, since the temperature at which Nitrate of Silver decomposes is far above its melting point.

Nitrate of Silver which has been much decomposed in melting, produces a great peculiarity of development. In the Positive glass process the whites are often solarized, and appear blue by reflected light; whilst in the Negative process the image is highly intense, with over-action in parts like the sky, and the film usually fogs slightly towards the end of the development: on applying the developer the whole picture starts out instantly, and the solution of Pyrogallic Acid becomes muddy instead of assuming by degrees the colour of sherry wine. These effects are not unlike those previously described as due to certain kinds of organic matter in the bath, the reduction of Silver by the developer being in both cases facilitated.

CHAPTER VII.

ON POSITIVE AND NEGATIVE COLLODION PHOTOGRAPHS.

The terms "Positive" and "Negative" occur so frequently in all works upon the subject of Photography, that it will be impossible for the student to make progress without thoroughly understanding their meaning.

A Positive may be defined to be a Photograph which gives a natural representation of an object, as it appears to the eye.

A Negative Photograph, on the other hand, has the lights and shadows reversed, so that the appearance of the object is changed or negatived.

In Photographs taken upon *Chloride of Silver*, either in the Camera or by superposition, the effect must necessarily be Negative; the Chloride being *darkened by luminous rays*, the lights are represented by shadows.

The following simple diagrams will make this obvious.

Fig. 1 is an opaque image drawn upon a transparent ground; fig. 2 represents the effect produced by placing it

Fig. 1.

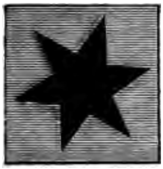


Fig. 2.

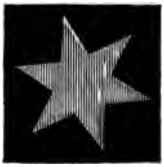
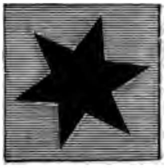


Fig. 3.



in contact with a layer of sensitive Chloride and exposing to light; and fig. 3 is the result of copying this negative again on Chloride of Silver.

Fig. 3 therefore is a Positive copy of fig. 1, obtained by means of a Negative. By the first operation the tints are reversed; by the second, being reversed again, they are made to correspond to the original: hence the possession of a Negative enables us to obtain Positive copies of the object, indefinite in number and all precisely similar in appearance. This capability of multiplying impressions is of the utmost importance, and has rendered the production of good Negative Photographs of greater consequence than any other branch of the Art.

The same Photograph may often be made to show either as a Positive or as a Negative. For instance, supposing a piece of silver-leaf to be cut into the shape of a cross and pasted on a square of glass, the appearance presented by it would vary under different circumstances.

Fig. 1 represents it placed on a layer of black velvet; fig. 2 as held up to the light. If we term it Positive in the first case, *i. e.* by reflected light, then it is Negative in the second, that is, by transmitted light. The explanation is obvious.

Fig. 1.

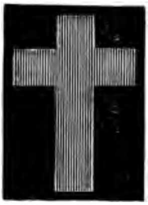
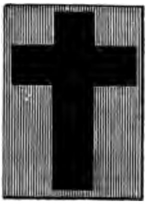


Fig 2.



Therefore to carry our original definition of Positives and Negatives a little further, we may say that the former are usually viewed by reflected, and the latter by transmitted light.

All Photographs however cannot be made to represent both Positives and Negatives. In order to possess this capability, it is necessary that a part of the image should be transparent, and the other opaque *but with a bright surface.* These conditions are fulfilled when the Iodide of Silver upon Collodion is employed, in conjunction with a developing agent.

Every Collodion picture is to a certain extent both Negative and Positive, and hence the processes for obtaining both varieties of Photographs are substantially the same. Although however the general characters of a Positive and a Negative are similar, there are some points of difference. A surface which appears perfectly opaque when looked down upon, becomes somewhat translucent on being held up to the light; hence, to give the same effect, the deposit of metal in a Negative must be proportionally thicker than in a Positive; otherwise the minor details of the image will be invisible, from not obstructing the light sufficiently.

With these preliminary remarks, we are prepared to investigate more closely the *rationale* of the processes for obtaining Collodion Positives and Negatives. All that refers to paper Positives upon Chloride of Silver will be treated in a subsequent Chapter.

SECTION I.

On Collodion Positives.

Collodion Positives are sometimes termed *direct,* because obtained by a single operation. The Chloride of Silver *acted upon by light alone,* is not adapted to yield direct Positives, the reduced surface being dark and incapable of representing the lights of a picture. Hence a developing agent is necessarily employed, and the Iodide of Silver substituted for the Chloride, as being a more sensitive preparation. Collodion Positives are closely allied in their nature to Daguerreotypes. The difference between the two consists principally in the surface used to sustain the sensitive layer, and the nature of the substance by which the invisible image is developed.

In a Collodion Positive the lights are formed by a bright surface of reduced Silver, and the shadows by a black background showing through the transparent portions of the plate.

Two main points are to be attended to in the production of these Photographs.

First, to obtain an image distinct in every part, *but of comparatively small intensity.*—If the deposit of reduced metal be too thick, the dark background is not seen to a sufficient extent, and the picture in consequence is deficient in shadow.

Secondly, to *whiten* the surface of the reduced metal as much as possible, in order to produce a sufficient contrast of light and shade. Iodide of Silver developed in the usual way presents a dull yellow appearance which is sombre and unpleasing.

The Collodion for Positives.—Ordinary Collodion iodized for Negatives and giving a thick yellow film, usually fails in taking good Positives. If the exposure in the Camera be sufficiently long to impress dark shadows, the lighter parts of the image develope with such rapidity that the gradation of tone is lost by excessive deposit of Silver. The addition of Nitric Acid to the Bath is to a certain extent a remedy, inasmuch as it lessens the intensity of the reduction and gives the Silver a sparkling appearance; nevertheless Positives taken in this way are always unpleasing, and cannot be compared with a good Daguerreotype in softness and delicacy.

A better class of picture may often be obtained by diluting down a sample of Collodion with Ether and Alcohol until it gives a pale-bluish film in the Bath. The proportion of Iodide of Silver being in that case small, the action of the high lights is less violent, and the shadows are allowed more time to impress themselves.

The employment of a very thin film for Positives is not invariably a successful process. The particles of the Iodide of Silver being closely in contact with the glass, unusual care is required in cleaning the plates in order to avoid stains; and as the amount of free Nitrate of Silver retained upon the surface of the film is small, circular patches of imperfect development, causing blue and green stains, are liable to occur, unless the reducing agent be scattered evenly and perfectly over the surface. Also if free Iodine or organic substances which have a retarding effect on the action of light be present to a considerable extent, the Collodion will not work well with a small proportion of Iodide: in such a case a creamy and dense layer of the sensitive Salt is required, to give a sufficient power of resistance.

In attempting to dilute down the Nitrate Bath at the same time with the Collodion, we gain in some respects an advantage. Excess of development is obviated, and the picture shows well on the surface of the film. The employment of a very weak Nitrate Bath (twenty grains of Nitrate of Silver to the ounce of water) in the Positive process is not however advisable on the whole. It becomes necessary, on account of the small quantity of Silver present, to exclude all free Nitric Acid, and even to avoid the employment of a Collodion too highly tinted with Iodine. On the other hand, with a strong Nitrate Bath, and a tolerably dense film of Iodide of Silver, a better result is often secured by the use of Nitric Acid, as will presently be shown.

These and other like processes, in which films of Iodide only are employed, have now been almost superseded by others, founded on a peculiar property which *Bromide* possesses when added in moderate proportion to an ordinary iodized Collodion. It alters the molecular state of the Silver reduced during development, rendering it metallic: the image also is superficial, and sufficiently translucent to give a perfect gradation of tone.

When Bromide is employed, in conjunction with Sulphate of Iron as a developer, the quality of the Pyroxyline is not of the same importance as in the case of pictures taken with a simply iodized Collodion. It has however been pointed out to the Author since the last edition of this Work was published, that his formula for Pyroxyline is better fitted for Negatives than for Positives. The peculiar quality of producing a vigorous image, imparted by the use of an excess of Oil of Vitriol in the Nitro-Sulphuric Acid, is an objection in the case of Positives, since it increases the opacity of the high lights and lowers their colour. In this Edition, therefore, the old formula for Nitro-Sulphuric Acid, containing equal bulks of Sulphuric and Nitric Acid, will be given in preference to that in which the proportions are as three to one.

To produce a very faint and superficial image, a *weak* Nitro-Sulphuric Acid must be used for the Pyroxyline (p. 114), but the objection is that after a certain point of dilution with Water, a quality of Pyroxyline is obtained, which becomes *opaque* on drying. This is comparatively immaterial when transparent varnish is applied to the image, but it spoils the appearance of the picture when mounted without varnish, as is sometimes preferred.

With regard to the quantity of Bromide which may be introduced, the operator should be guided by the aspect of the developed image. If, when exposed long enough to form the shadows, the high lights appear too dense, more Bromide must be added: whilst, on the other hand, if the Positive is grey and feeble, *and this defect is not due to over-exposure*, the proportion of Bromide may be reduced. The American operators, who are very successful with Collodion Positives, employ more Bromide than is recommended in this Work, but their Pyroxyline may possibly be made in a different manner.

One effect produced by Bromide in Positive Collodion, is seen in keeping the lines of the picture sharp and clear during development. When the Bath is strongly acidified with Nitric Acid and a simply iodized Collodion is employed, the image is often *blurred* by an irregular deposit of Silver, giving an appearance like defective focussing. With Collodion containing mixed Iodide and Bromide in the proper proportions, this does not so frequently happen, the image remaining clear and free from stains.

Does Bromide increase or diminish the sensitiveness of the film to a weak light? This is a question which can only be answered by considering the chemical state of the Collodion, Bath, and developer. With a weak solution of Pyrogallic Acid as a developer, and a dilute Bath, Bromide seems to *diminish* the sensitiveness considerably, but this appearance is delusive, since the latent image is really present, and simply requires a stronger reducing agent and more Nitrate of Silver to bring it out. On increasing the strength of the Bath therefore and using Sulphate of Iron as a developer, the whole of the details will show themselves after a minimum of exposure in the Camera.

There are states of Collodion also in which the use of Bromide may *increase* the sensitiveness, viz. when decomposition has taken place. Every practical operator learns by experience that Positive Collodion containing Bromide does not lose sensitiveness after iodizing in the same rapid manner as Negative Collodion prepared without Bromide. Doubtless the difference in the developing solutions—Sulphate of Iron in the one case and Pyrogallic Acid in the other—has something to do with this result; but a peculiar action of the Bromide in rendering the Collodion independent of organic changes due to keeping after iodizing must be allowed.

A comparatively newly-iodized Collodion is seldom in the best possible state for taking Positives; for if it be colourless or nearly so, the plates will show clouding after development. By keeping the Collodion for several weeks, a portion of the Iodine is liberated, which has a great effect in giving brilliancy to the picture, by preserving the shadows from the reducing action of the developer.

The Nitrate Bath.—An ordinary neutral thirty-grain solution of Nitrate of Silver, such as is used for Negatives, may be employed also for Positives, and especially so if the Collodion be purposely kept after iodizing until it assumes a yellow tint, and liberates enough Iodine to prevent the clouding which might otherwise take place in the absence of acid. Negative Baths, however, which contain

Acetate of Silver, or any kind of organic matter, or which have been made from Nitrate of Silver previously decomposed by strong fusion, are not well adapted for Positives, since these conditions promote solarization, a defect which shows itself in Positives by discoloured whites on the most exposed parts of the film.

When the Nitrate Bath is made purposely for direct Positives, it is always better to acidify it with Nitric Acid rather than with Acetic Acid, as used for Negatives. The Nitric Acid diminishes the density of the deposited image, renders it whiter and more metallic, and assists in preserving the clearness of the plate. The mistake has sometimes been made of using too much Acid in proportion to the strength of the Bath, which not only lessens the sensitiveness of the film, but also, as before shown, promotes a blurring of the image, and a fogging from irregular reduction. Even with a Collodion containing Bromide, there will be a tendency to staining and imperfect development, if the amount of Nitric Acid be carried as far as is sometimes recommended, in the case of a Bath of thirty grains to the ounce.

Many successful operators use a Bath of forty grains to the ounce for Collodion Positives, in order to shorten the exposure in the Camera, and give brilliancy to the image. This solution will bear a far larger addition of Nitric Acid than the ordinary Bath of thirty grains; and, always supposing Bromide to be present in the Collodion, satisfactory pictures may be obtained with a quantity of Nitric Acid as large as two minims to the ounce. Neither is the sensitiveness very much impaired by the excess of Acid; thus showing how many conditions have to be taken into account in considering the formation and development of the Collodion picture. With a Bath very strongly acidified, it would be impossible to get any result if the proportion of Nitrate of Silver and Iodide of Silver in the Collodion film were both reduced to one-half. The Acid and Nitrate of Silver must, in fact, be balanced against each other, and when the Collodion film is lessened in opacity, the developer must be considerably strengthened, otherwise the latent image, although actually present, cannot be made to appear in the half-shadows.

The Author's experience is not favourable to the employment of a forty-grain Bath in the Positive glass process as far as beginners in the Art are concerned. He finds that there are fewer failures when the Bath contains thirty grains of Nitrate of Silver to the ounce, and is only slightly acid. Stains of reduced Silver at the edges of the plate are not easily avoided in the case of a strong and acid Bath, and if the developer is too weak, there are metallic spangles on the shadows.

A Positive Nitrate Bath, containing both Alcohol and Nitric Acid, ought never to be exposed to the light. The writer has observed that when this precaution is neglected, *oxidation* of the organic substance soon ensues, and the Nitric Acid disappears, leaving the solution in a state which produces clouded pictures.

Developers for Collodion Positives.—In the case of a Collodion which does not contain Bromide, Pyrogallic Acid is occasionally employed as a developer. When mixed with Acetic Acid, as is usual for Negative pictures, it produces a surface which is dull and yellow, but this may be obviated by substituting a small quantity of Nitric Acid for the Acetic (Pyrogallic Acid, 2 grains; Nitric Acid, 1 drop; Water, 1 ounce). The surface produced by Pyrogallic Acid with Nitric Acid is lustreless, but very white, if the solution be used of the proper strength. On attempting to increase the amount of Nitric Acid the deposit becomes metallic, and the half-tones of the picture are injured; since Pyrogallic Acid, although an active developer, does not allow of the addition of mineral acid to the same extent as the Salts of Iron: it requires also, when combined with Nitric Acid, a fair proportion of Nitrate of Silver on the film, or the development will be imperfect in parts of the plate, producing green and blue stains; if such stains occur, a few drops of a solution of Nitrate of Silver may be added to the developer before use.

Sulphate of Iron.—This salt is a more energetic reducing agent than the last, and is better fitted for employment with a Collodion containing a portion of Bromide, the action of Bromide being to retard the development. To produce by means of Sulphate of Iron a dead white tint with absence of metallic lustre, it may be used in conjunction with Acetic Acid.

The addition of *Nitric Acid* to Sulphate of Iron modifies the development, making it more slow and gradual, and producing a bright sparkling surface of reduced Silver. Too much of this acid however must not be used, or the action will be irregular. The Nitrate Bath also should be tolerably concentrated, in order to compensate for the retarding effect of Nitric Acid upon the development. The blue and transparent films of Iodide of Silver, are not well adapted for Positives to be developed in this way. Such films require the most vigorous developer possible; Acetic Acid should therefore be used instead of Nitric Acid.

Protonitrate of Iron.—This salt is remarkable as giving a surface of brilliant metallic lustre without any addition of free acid. Theoretically, its action may be considered as closely corresponding to that of Sulphate of Iron with Nitric Acid added. There are however slight differences between them, which are in favour of the Protonitrate, as regards the colour of the image.

The reducing powers of *Protoxide* of Iron appear to be in inverse ratio to the strength of the acid with which it is associated in its salts; hence the *Nitrate* is, of all the Protosalts of Iron, by far the most feeble developer, and is seldom used alone in Photography. In the case of a Bromo-Iodized Collodion very little dependence must be placed upon the Protonitrate of Iron as far as reducing Metallic Silver is concerned, but it may be added to solution of Sulphate of Iron when the peculiar metallic tone which it imparts, is desired. Beginners often fail in using this developer, from not allowing a sufficient excess of the Sulphate of Iron in its preparation, and from supposing that the Protonitrate is equally as strong a reducing agent as the Protosulphate, whereas it is at least twenty times weaker.

The Tone and Colour of Positives.—The same chemicals yield such different results in the hands of various operators, that some have spoken of manipulation and practice as more essential than theory. Doubtless the exact time of exposure in the Camera is important, because a short exposure always produces an image of a whiter colour and more transparent shadow than a long exposure. In the case of Negatives, the image, viewed by transmitted light, is often of a jet-black when under-exposed, but of a ruby-red when over-exposed. So in Positives, it is always brighter and more metallic when the action of the light is stopped at the proper time. There are other causes of variation in the colour of the Positive image, such as changes in the actinic intensity of the light; and the operator may expect to produce a better quality of picture when the light is strong.

The gradation of tone in Collodion Positives will also be affected by the mode in which the light falls upon the subject; for when it possesses great actinic power, there is always a tendency to an excessive reflection from the high lights; and if this be not counteracted by an arrangement of curtains, to be described in the second part of the Work, it will require the utmost attention to the state of the chemicals, to prevent excess of intensity, and loss of good shading.

The mode of developing the Positive image has an effect upon the gradation, independently of the exposure, or of peculiarities in the Collodion. The theory is as follows: —When the Nitrate of Silver is present upon the film in large quantity relatively to the Sulphate of Iron, the tendency is to give great contrast of image, and to produce a bold picture, which appears to stand out from the glass. The deposit of Silver in such a case falls more abundantly upon the high lights, and less so upon the shadows, so that the shading in the face and lighter parts is often lost. On the other hand, when the quantity of Nitrate of Silver is much reduced in relation to the Sulphate of Iron, the image developes more slowly, and is soft and full of half-tone: in extreme cases the high lights are not sufficiently opaque, and the features of the sitter, after backing up with the black varnish, are those of a Negro. This rule applies to every kind of developed picture, and the practical inference from it is, that when the Positive is too vigorous, and the details in the face are lost, *a large quantity* of developing solution should be scattered over the film so as to wash off a portion of the free Nitrate of Silver. Experimental trial will convince the operator how extremely minute is the proportion of Nitrate of Silver actually required for the formation of the image; but no exact directions can be given, since the quantity will vary with the density of the sensitive film, the brightness of the light, the amount of retarding acid, and the strength of the developer.

Fixing Agents for Positives.—Hyposulphite of Soda is not usually employed for fixing Collodion Positives, since it contains Sulphur, and is somewhat unstable; hence the image is liable to be superficially darkened to an appreciable extent. Cyanide of Potassium is free from this objection, and always produces a whiter picture than Hyposulphite. The strong solvent powers of Cyanide of Potassium must be borne in mind, when using it as a fixing agent; for if the solution be too concentrated or allowed to remain a long time upon the plate, the middle tints first become whitened from conversion into Cyanide of Silver, and immediately afterwards begin to dissolve. It is also the opinion of many who employ *commercial* Cyanide, that it should not be used without first adding a few crystals of Nitrate of Silver to lessen its solvent effect upon the half-shadows. Neither should the plate be exposed to a strong light whilst the Cyanide is upon it, as the action of light favours the conversion of the image into Cyanide of Silver.

A Process for Whitening Positives by Corrosive Sublimate.—In place of brightening the Positive image by modifying the developer, it was proposed some time since by Mr. Archer to effect the same object by the use of the Bichloride of Mercury.

The image is first developed in the usual way, fixed, and washed. It is then treated with the solution of Bichloride (thirty grains dissolved in an ounce of hot water), the effect of which is to produce almost immediately an interesting series of changes in colour. The surface first *darkens considerably*, until it becomes of an ash-grey, approaching to black; shortly it begins to get lighter, and assumes a pure white tint, or a white slightly inclining to blue.

The *rationale* of this reaction appears to be, that the Chlorine of the mercurial salt divides itself between the Mercury and the Silver, a portion of it passing to the latter metal and converting it into a Protochloride. The white powder is therefore probably a compound salt, as is further evidenced by the effects produced on treating it with various reagents.

Positive Photographs whitened by Bichloride of Mercury have usually more or less of a bluish tone, but this may be overcome by associating other chemicals with the Bichloride. A more serious objection is the instability of the picture after whitening, since it has been shown that these images are liable to fade unless special precautions be taken.

SECTION II.

On Collodion Negatives.

As in the case of a direct Positive we require an image which is *feeble* though distinct, so, on the other hand, for a Negative, it is necessary to obtain one of considerable intensity. In the Chapter immediately following the present, it will be shown that in using glass Negatives to produce Positive copies upon Chloride of Silver paper, a good result cannot be secured unless the Negative is sufficiently dark to obstruct light strongly.

There are various conditions affecting the formation and development of a Photographic Negative, which ought to be studied by one who aims at perfection in the Art. Some of these are—the quality of the light at the time of taking the picture, the focal length and aperture of the Lens, the state of the atmosphere, etc. To meet the different cases which may arise, the Collodion, the Nitrate Bath, and the developing solution may each or all be considerably modified.

With regard to the first of these conditions we may observe that the mode in which a Negative developes, and its colour when the process is completed, vary much with the actinic intensity of the light. Pictures taken by a short exposure in a strong light, develope easily under the Pyrogallic Acid. The first deposit of Silver is often of a red colour when held against the light, and this influences the subsequent precipitation (see p. 40), so that the Negative continues to darken until the whole of the Nitrate of Silver in the film has been decomposed. When examined after fixing, it shows a plum-colour or yellow bloom by reflected light, and is often brown by transmitted light. In dull wintry weather, on the contrary, and especially when the atmosphere is loaded with aqueous vapour, the Negative picture is slow in appearing under the action of the developer, and the image first formed is rather of a violet blue than of a red colour. In consequence of this, the subsequent deposit of Silver is likewise of a violet-blue, and a much longer time is expended in bringing the development up to the proper point. The particles of precipitated Silver are always larger when the reducing process is slow, and thus Negatives taken in a bad light often prove in printing to be less intense than they appear, whereas those taken in a bright light are usually more intense chemically than visually.

When the strength of the light falls very low indeed, as, for instance, in working in a room covered in with glass of a greenish tint, fatal to quick Photographic action, the darker parts of the picture fail to impress the film, and the Negative shows only patches of black and white; or, with a more sensitive collodion, the whole picture appears, but is extremely feeble and indistinct, a deposit of Silver falling upon the shadows and giving a cloudy aspect. On the other hand, in a light of extreme brilliancy, reddening from solarization is to be apprehended, the actinic rays being reflected from the high lights of the subject in a proportion greater than from the shadows: this may happen especially with a sky free from fleecy clouds, which when present have a great effect in illuminating the shadows and diminishing excessive contrast. When solarization of Negatives occurs from great intensity of light, the image often starts out almost instantaneously on applying the Pyrogallic Acid, and after fixing by the Hyposulphite of Soda exhibits an intensely red appearance of the high lights, with a steel-blue colour of the same parts viewed by looking down upon them.

We notice in the second place the focal length and aperture of the Lens, as a condition influencing the quality of the developed Negative. If, for instance, two Cameras be pitched side by side, at the same view, one being a Stereoscopic instrument with a single Lens of 4½-inch focus, and the other fitted with a twenty-inch Lens, suitable for glasses of twelve inches diameter, the plates, even when properly exposed, will behave differently under the action of the developer, the Stereoscopic picture showing by far the greater intensity, contrast of tint, and tendency to solarization. The relative power of the Lenses makes the difference, the short-focus Lens producing a brilliant image which impresses the sensitive film in less than a third of the time required by the other. A second experiment, equally instructive, may be made by surrounding a group of statuary with a dark drapery, so as to produce a strong contrast of light and shade. On copying such an object with the full aperture of a short-focus Lens, it will be found almost impossible, unless the composition of the Collodion be modified in a manner presently to be explained, to get the whole of the picture simultaneously. Either the whites will be well rendered, and the blacks wanting, or by a longer exposure the shadows will be well brought out, but the lights solarized. Now take the same Lens and cut down the effective aperture by a middle-sized diaphragm, allowing proportionally longer time in the Camera, when a perfect Negative will be produced. This rule, then, may be stated as follows:—A Camera image of great actinic intensity often produces a Collodion Negative with exaggerated contrast of light and shade, and conversely an image of low intensity tends to give a picture which is too uniform, and deficient in extreme tints. Availing himself of this knowledge, the skilful operator alters the size of his diaphragms according to the quality of picture desired, and remedies solarization by diminishing the supply of light.

The amateur, on commencing Photography, is often at a loss to understand apparent discrepancies in the formulæ employed by various operators, and in their general mode of working. In one instance a plate of twenty inches by seventeen is developed to the full intensity with a single application of the reducing agent; in another, a Negative of half that size is found to require repeated treatment with Pyrogallic Acid and Nitrate of Silver, and to occupy ten or fifteen minutes in reaching the full opacity. Supposing the Lens and chemicals to be the same in each case, the difference may depend upon *the character of the subject.* When a distant landscape is Photographed, a large number of rays of light are concentrated upon the film: but if an object like an old picture or a faded drawing be copied without any reduction in size, the light is very feeble. No careful timing of the exposure will cause two such Negatives to develope in the same way, because the long-continued action of a weak light in the Camera does not correspond to the shorter action of an intense light. The molecules of Iodide of Silver are differently affected in the two cases, and consequently they behave differently when treated with the mixture which constitutes the developer.

The Collodion for Negatives.—A perusal of the First Section of the last Chapter (p. 114) will show that the properties of Negative Collodion vary much with the mode of preparing the Pyroxyline. Upon this subject it is not necessary to enlarge at present, since it will again be alluded to in the Chapter on dry Collodion. Distinguishing terms however are always useful, and hence we propose to speak of Pyroxyline *with*, and Pyroxyline *without* organic reactions towards the Salts of Silver; the former being the variety which yields the intense Negative images.

Pyroxyline without organic reactions may be expected to give the greater sensitiveness of the two, and the better keeping qualities after iodizing. It is however difficult to use it in consequence of the increased liability to fogging and spots of all kinds (p. 48). Also when the intensity and contrast of the image are too small, as frequently happens with such Collodion, they cannot easily be increased, whereas excessive intensity may readily be reduced. The Pyroxyline *with* organic reactions is therefore preferred by the majority of operators.

For the sake of greater simplicity, the Author has given only one formula for Negative Pyroxyline in the first Chapter of the second or practical division of the Work. This formula appears to answer well for a normal Collodion, applicable to all purposes. Those however who wish to prepare a Pyroxyline suitable for any one especial kind of work, may read the section in Part II., on portraits, landscape photography, and copying, where they will find the subject examined more fully.

Independently of the Pyroxyline, Negative Collodion may be described as of two kinds, the simply iodized, and the *Bromo*-iodized Collodion. Each has its advantages and likewise its defects. The first gives the greater sensitiveness, and also the greater intensity, but it is more liable to spots and markings, and the purity of the chemicals is of greater importance than when bromo-iodized Collodion is employed.

Let us examine the above points more minutely. It must be allowed that the addition of a Bromide to Negative Collodion impairs the sensitiveness. Much indeed depends upon the mode of developing, but even when the reducing agent is strong, and the Nitrate of Silver abundant, the Bromo-iodized Collodion is still inferior in that respect. If such a Collodion be found on trial to yield a picture in eight seconds, a pure, simply iodized Cadmium Collodion, will probably give the same picture in five seconds. Hence in the dull winter months, many are necessitated to employ Iodides alone, who at more favourable times use combinations of Iodide and Bromide.

The excessive sensitiveness of simply iodized Collodion however is not seen in perfection, unless all the materials are pure, and hence some have stated that the addition of a small portion of a Bromide increases the sensitiveness. Experiments leading to such a conclusion were probably made with a Collodion which from organic decomposition of the Pyroxyline or other causes, had acquired the property of producing an intense negative, and in this case the action of the Bromide as already shown at page 145 is peculiar. A Pyroxyline without strong organic reactions is proper for the most sensitive iodized Collodion, and the Ether must also be very pure. When this extreme purity of the Ether cannot be secured, Iodide of Cadmium should be used in place of Iodide of Potassium, to preserve the fluid in a neutral and colourless condition. The manufacturer of Collodion who examines its properties shortly after its preparation finds little or no difference between the Iodide of Potassium and the Iodide of Cadmium. The purchaser however usually esteems the latter to be superior as regards sensitiveness, because the plain Collodion has often been kept for a time before he obtains it, and has acquired the property of displacing Iodine: hence with the Potassium iodizer the colour changes quickly to orange-yellow, and the action of the light is retarded. Iodide of Cadmium, in consequence of its stability, would have superseded the other Iodides, had it not been for its glutinizing action on Pyroxyline, a serious objection in covering large surfaces of glass.

The effect of Bromide in diminishing the *intensity* of the image has already been considered in the section on Positives. It is often used for the same purpose in Negative Collodion, because when the light is strong and the Lens powerful, the intensity and contrast may be in excess, and if so, either a black and white picture without middle tints, or a red picture defective from solarization will be obtained. The Bromide effectually remedies both these causes of failure; frequently indeed it originates an error in the opposite direction. On looking at a Negative taken with a Bromo-iodide Collodion, we see that the peculiar metallic effect given by the Bromide is most evident in the half-shadows of the picture, where the light acts feebly. Provided there be a sufficiency of light, enough intensity will be obtainable in presence of Bromide, but when the light is too much reduced, the image will be rendered weak and translucent thereby. A Negative must possess a certain amount of intensity, and also a proper colour, if it is to possess what the Photographer terms "good printing qualities." These qualities cannot be secured by merely pushing the development and piling up particles of metallic Silver: much will depend upon the colour of the image in its early stage, which should be of a soft red, and appearing nearly homogeneous when magnified. The employment of Bromide should be suspended when the particles of Silver become large and crystalline, since this condition of image is too permeable to the chemical Light in the process of printing.

The use of Bromides in Negative Collodion must be regulated by the nature of the Pyroxyline, as well as by the brilliancy of the light. The more marked the organic reactions of the Pyroxyline, the greater the proportion of Bromide admissible. This rule is the same as that laid down for Collodion Positives (p. 144), and the directions are to examine the Negative, and if the contrast between the high lights and the shadows is too marked, to increase the quantity of Bromide. There are varieties of Pyroxyline which will not bear any addition of Bromide, the contrast of the image being too small, even with simple Iodide.

Apart from all considerations of density of Negative depending either upon the light or the Pyroxyline, it must be admitted that the employment of Bromide in Negative Collodion is most desirable for other and distinct reasons. The latent image produced in the Camera appears to be of a more definite description upon a bromo-iodized than upon a simply iodized Collodion. In the case of the latter, disturbances of all kinds are apt to arise during development; the deposit is defective in one part of the plate, and irregular in another, so that to secure a Negative free from all blemish is a rare occurrence. Much indeed depends upon the skill of the operator and the purity of his chemicals, but this does not lessen the value of the Bromide, which undoubtedly exercises a remarkable influence in preventing, not only over-action of light, but likewise transparent markings, vertical lines, and spots of all kinds. Iodide of Silver, when associated with Bromide, receives the molecular modification in the Camera somewhat tardily, but when once impressed, it retains the image with greater force, and is not equally liable to the reception of false images from moisture or traces of organic matter upon the glass (p. 50).

Although in anticipation of our subject, we may here remark in addition, that those minor decompositions and impurities in the Negative Nitrate Bath, which so frequently disturb the image in the case of a simply iodized Collodion, will not produce the same effect when the film contains Iodide and Bromide conjoined. To prove the truth of this assertion, the Writer on one occasion collected several impure Nitrate Baths, none of which would yield a perfect Negative with ordinary Collodion, and yet he succeeded in every case in taking a good impression with Bromo-iodized Collodion. Bromide therefore may be viewed as a useful adjunct when retarding impurities of various kinds are present, against which the unassisted Iodide would be unable to contend.

Changes in Negative Collodion after Iodizing.—All Collodion loses sensitiveness more or less after iodizing, and especially so when the Pyroxyline is unstable and liable to part with a portion of its Peroxide of Nitrogen; also when the Ether is impure and in a state to absorb Oxygen. Practically we esteem a Collodion iodized with Iodide of Cadmium as uniform in properties, since if the chemicals are of good quality it will retain its sensitiveness nearly unchanged for twelve months after iodizing. Next in stability to the Cadmium Collodion stands the Bromoiodized Collodion, which remains unchanged for a far longer time than a simply iodized Collodion (p. 127), and will retain a fair share of sensitiveness for many weeks.

Negative Collodion produces as a rule a more intense image when kept for a time in the iodized state, and this is true not only of Collodion iodized with the alkaline Iodides, but also of that containing Iodide of Cadmium. Bromoiodized Collodion also gains in intensity as it gradually decomposes, and the quality of the Negatives is usually better after a few weeks' keeping than at first; they have more of a red or black tone, and exhibit greater contrast.

When alkaline Iodides are used, both the simple and the Bromo-iodized Collodion become more limpid by keeping. This is an advantage in coating full-sized plates, and since the setting powers of the Collodion are lessened, it becomes far easier to cover a large surface before gelatinization ensues. Old iodized Collodion of this kind is likewise more porous and permeable by the developer than newly iodized, which affords another reason why it is especially suitable for large plates.

Clearness of the transparent parts in Negatives, with increased sharpness of outline, are both effects of keeping Collodion after iodizing. These peculiarities, as well as the comparative absence of spots and markings, are due partly to the "organic reactions" developed in old Collodion, and partly to the acid state of the film, when the Collodion is brown from free Iodine.

On keeping simply iodized Negative Collodion for a much longer time, the amount of free Iodine often becomes so great that the colour deepens to a red, and a portion of

Nitric Acid is liberated on dipping the film into the Bath, sufficiently large to lower the density of the Negative, and make it grey and metallic. In this state, with sensitiveness and intensity both reduced to a minimum, the only remedy is to add an essential oil, like the Oil of Cloves, which, having an affinity for Oxygen, neutralizes the action of the Iodine, and restores the sensitiveness partially, and the intensity entirely, so that the Negative developes with a full amount of bloom and creaminess, as before.

The Negative Nitrate Bath.—In the Second Section of the last Chapter the chemistry of the Nitrate Bath was explained, with the action of organic substances upon it, and the marked effect which they produce upon the development of the Negative image.

Supposing the Nitrate of Silver to be chemically pure, a question arises as to the proper state of the Negative Bath as regards strength, acidity, presence of Acetate of Silver, etc. On these points opinions are divided. Much depends upon the quality of the Collodion, and therefore the observations now to be made may be said to apply principally to the use of a simply iodized Collodion prepared by the formulæ given in this Work, and not to a Collodion containing both Bromide and Iodide.

Negative Baths have been used with as much as forty grains of Nitrate of Silver to the ounce of water. When the Collodion is feeble and contains Bromide, an increase both of sensitiveness and intensity is thus gained, but with ordinary Collodion, thirty grains of Nitrate of Silver to the ounce of water is quite sufficient, and any proportion beyond this would only add to the rapidity of development and tendency to staining in hot weather. When a Bath, originally made with thirty grains of Nitrate of Silver to the ounce of water, has been much used, the proportion of Nitrate will be found on analysis to have been reduced to twenty-five grains to the ounce. Ordinary Collodion dipped in such a Bath produces a less creamy film than usual, and the sensitiveness may be found to be diminished.

The reaction of the Bath to test-paper ought to be either neutral or slightly acid, the presence of free alkali being always injurious. A neutral Bath produces a more dense Negative in dull weather, but is apt to give solarization in bright sunshine. The presence of Acetic Acid obviates this in great measure. An impression is not uncommonly entertained that any Acid in the Bath greatly diminishes the sensitiveness. With the Collodion described in Part II., the Writer does not find such to be the case, and therefore in hot weather, and with a neutral colourless Collodion, he recommends that Acetic Acid should be used in the Bath to prevent rapid discoloration on applying the developer. A minim of the Glacial Acid may be dropped into each four or five ounces, if the subject be well lighted. In using an Acid Bath, however, the developer should be proportionally strengthened if the temperature or the light afterwards fall.

The use of *Nitric Acid* in the Negative Bath has been usually condemned as interfering with the precipitation of the Silver in the *opaque* form, but in this instance also everything depends upon the Collodion and the light. Pyroxyline with organic reactions tends so strongly to produce a brown or red image in bright sunshine, that the Collodion can be worked successfully in a Bath containing a trace of Nitric Acid. In circumstances favourable to rapid development and solarization, such as Stereoscopic Photography with Lenses of a short focus, the presence of a minute quantity of Nitric Acid is often a positive advantage, and no marked effect in preventing the development of details in the shadows will be perceived.

The employment of *Acetate of Silver* in the Bath met with much favour in the early days of Photography, but principally so because the preparation of pure Nitrate of Silver and the chemistry of Collodion were not understood. There is in fact an impurity common in commercial Nitrate of Silver (see p. 135) which lowers the density of Negatives, and since Acetate always increases the density, its use has been found in such cases to be an improvement. So, again, Pyroxyline made at low temperatures and in weak Acids produces a violet image (p. 114), and hence Acetate of Silver, which changes the colour from blue to red, increases the intensity. When we add to this the fact that the presence of Acetate frees the Bath effectually from Nitric Acid, and thus enables a Collodion to be used which has been kept a long time, and is very brown from excess of free Iodine (p. 160), it is not difficult to understand why it has been so extensively employed. If pure recrystallized Nitrate of Silver be selected in the first instance, and proper attention paid to the state of the Collodion, both as regards the length of time it has been kept after iodizing, and the quality of the Pyroxyline, full intensity of Negative may be obtained without the use of Acetate, even under somewhat unfavourable conditions.

The objections to the employment of Acetate of Silver in the Bath are that it renders the solution more liable to change by keeping, favours red solarization in sunny weather, and at high temperatures increases the chance of spots, markings, and discoloration of the developer on touching the film.

Developing Solutions for Collodion Negatives.—Three formulæ are given in Part II., each of which has its advantages. The first contains Pyrogallic Acid with Acetic Acid; the second, Pyrogallic Acid with Citric Acid; and the third, Sulphate of Iron.

Pyrogallic Acid with Acetic Acid is the form most commonly employed, the use of the Acetic Acid being to moderate the violence of the action, and to preserve those parts of the Iodide which have not been touched by light (p. 47). It has also the advantage of causing the solution to flow easily upon the film, thus forming a substitute for Alcohol, which would otherwise be required to prevent greasiness and streaks. The ordinary strength of the solution of Pyrogallic Acid is one grain to the ounce of Water, but as regards the quantity of Acetic Acid, the practice of operators varies. The intensity is greatest when the minimum proportion of about five minims to the ounce is used, but in this case a portion of spirit will be required in covering large plates. With a Negative Collodion giving abundance of intensity it is better in every respect to employ the full strength of acid, viz. from twenty to thirty minims to the ounce, by which the reduction will be rendered more even, and stains of irregular action prevented.

Although Pyrogallic Acid, being an organic or vegetable substance, is a reducing agent well calculated to produce an intense Negative image, yet its effect in this respect will vary much with the nature of the sensitive film. In the case of a simply iodized Collodion, Pyrogallic Acid produces an opaque, and Sulphate of Iron a translucent Negative, but with a Bromo-iodized Collodion the difference between the two developers is very slight, the particles of Silver being precipitated in the metallic state even with the organic developer. It is also necessary to bear in mind that when Pyrogallic Acid is employed with a Bromo-iodized Collodion, the strength of the solution must be at least three times greater than that before advised, otherwise the darker parts of the picture will not appear, unless the exposure in the Camera be very considerably increased.

Attention should here be drawn to the decomposition which commercial Pyrogallic Acid experiences by keeping. In the course of a very few days in hot weather the solution becomes yellow, and not only loses, in some measure, its power of developing the weakest radiations, but rapidly discolours the Nitrate upon the film. Solution of Sulphate of Iron also becomes yellow by keeping, but in this case no injurious effect results except in the weakening of the developer.

Pyrogallic Acid with *Citric Acid* may be viewed as a weaker reducing agent than the last, and one less likely to develope the dark shadows after a short exposure. Citric Acid, in fact, is an agent of far greater power in retarding reduction of Silver, than Acetic Acid, and three-quarters of a grain will be found more than equivalent to twenty minims of the latter. This property of Citric Acid is an advantage when working at high temperatures, as, for instance, in a tent heated by the direct rays of the sun. The ordinary developer then acts so quickly that it is impossible to cover the plate before the reduction begins, and the discoloration on touching the film is rapid, so that the pictures are almost invariably weak and red, with stains and spots. In this state of things a stronger Acid will be found serviceable, and although the ordinary proportions are twice as much of Pyrogallic Acid as of Citric Acid, yet in extreme cases, the relative amount of Acid may be doubled, and a grain of each constituent of the formula be dissolved in an ounce of Water. The solution will flow evenly over the film on adding Alcohol, and the image will not appear until after an interval of twenty or thirty seconds. At so high a temperature the reducing power of even a feeble developer will be quite enough to bring out the shadows.

Citric Acid in the developing solution changes the colour of the Negative from brown to blue, and in consequence the real intensity of the image is somewhat less than it appears. It also has a marked effect in preventing red solarization in a brilliant light, and in preserving the surface of the film from fogging. Hence it is particularly adapted for distant landscape views including sky and water, or for other subjects well lighted; whilst, on the other hand, it is not suited for working in a glass house in a bad light and in cold weather, not for copying works of art with long-focus Lenses, or for taking interiors. In all such cases we may anticipate, when using a developer containing Citric Acid, that the image in its early stage of development will be weak and metallic, showing nothing of that tone of red which is so essential to the proper continuance of the precipitation. There will also be a loss of half-tint from the reducing agent being too weak to bring out the darker portions of the image.

Pyrogallic Acid with Citric Acid forms a good developer for a Cadmium landscape Collodion. Free Iodine being absent from this Collodion, the film on leaving the Bath is nearly neutral, and no Nitric Acid is present (p. 132). Consequently the high lights over-act, and render the image very feeble unless the developer contain a stronger acid than Acetic Acid. Pyrogallic Acid with Citric Acid does not, however, form a good developer for a Bromo-iodized Collodion, since it is too weak to bring out the half-tones in presence of Bromide.

Sulphate of Iron is a developer of great power, and may be employed with advantage when its action is correctly understood. Being a substance belonging to the mineral kingdom, it is not favourably constituted for producing that *opacity* of image which is characteristic of Pyrogallic Acid; but on the other hand it is a much stronger reducing agent, and will bring out a perfect picture, when from some opposing conditions, the ordinary developer proves ineffectual.

In order that a Negative Collodion may be adapted for developing with Sulphate of Iron, it ought to be of that kind which gives abundance of intensity and strong contrast of image. It must likewise be a Collodion working clean and free from fogging, inasmuch as the Sulphate of Iron has a tendency to precipitate the Silver in an irregular manner upon the film greater than that of the Pyrogallic Acid. In a doubtful case it will be well to develope a trial plate with Pyrogallic Acid: if the picture prove feeble and cloudy, the use of Sulphate of Iron will be contra-indicated.

The state of the Nitrate Bath must also be considered in making choice of a developer. Newly prepared Baths which yield rather faint Negatives with Pyrogallic Acid, seldom succeed with Sulphate of Iron unless the Collodion contain Bromide: the image becomes rapidly fogged and is useless. Baths made from fused Nitrate of Silver; Baths containing Acetate; and old Baths contaminated with organic matter, can on the other hand be worked more successfully with Sulphate of Iron than with Pyrogallic Acid. The rule appears to be that if the solution is in a state for giving very red Negatives with great intensity and freedom from fogging, the inorganic developer will be the better of the two: for in that case the organic reactions of the film are already at their maximum, and hence, an organic developer like Pyrogallic Acid destroys the balance.

Depression of temperature is always an indication for the use of Sulphate of Iron, and in such a case its superiority is especially evident. When the thermometer sinks to 40° Fahrenheit, it will be found that the ordinary solution of Pyrogallic Acid and Acetic Acid acts very slowly, and, in the case of Collodion which has undergone a little organic decomposition, it does not bring out the dark shades effectually, so that on examining the Negative after fixing, it appears to have received an insufficient amount of exposure in the Camera. An increase in the strength of the solution, using more of the Pyrogallic Acid and less Acetic Acid, does not altogether remedy the defect, although it adds to the opacity of the parts which have received most light. The substitution of Citric Acid for the Acetic would weaken the reducing power, and be a positive evil. Nothing then remains but either to warm the Bath and developing room by a stove, or to employ the Sulphate of Iron.

The difficulty of securing a proper gradation of tone is especially felt, not only in cold weather, but also when the picture embraces a variety of objects which contrast strongly in their power of reflecting light. Pyrogallic Acid as a developer is apt either to destroy the definition in the light parts by producing absolute opacity of the Negative, or to exhibit all the effects of over-action of light and red solarization. In this way the folds of white drapery suffer, and the distance in landscapes is lost. Such subjects can be photographed successfully, either by using a feeble Negative Collodion destitute of organic re-actions (p. 155), by adding Bromide to an intense Collodion, or by developing with Sulphate of Iron. Monuments of white marble standing out against the sky, with cypress-trees in the background, have been well copied by using Sulphate of Iron; and although the Writer has seen equally good results obtained with Pyrogallic Acid, by giving a long exposure and working with a small aperture to the Lens—

yet he is satisfied that this can only be expected when the Bath and Collodion are in the most perfect working order, and that the Iron salt will ordinarily prove superior to the organic developer in such a case.

There are other causes of imperfect gradation of tone which Sulphate of Iron is employed to remedy. When, for instance, the atmosphere is yellow or murky, and no clouds exist to throw back the light into the shadows, it becomes very difficult to work a simply iodized Collodion successfully with Pyrogallic Acid: the blacks of the Negative are too opaque, and the shadows too transparent. A longer exposure in the Camera in this instance is only a partial remedy, because it invariably *flattens* the picture, destroying its rotundity and stereoscopic effect. The use of Sulphate of Iron is exactly adapted to meet the case, for it has great power in developing weak radiations, whilst at the same time it precipitates the Silver in a comparatively metallic and translucent form. The resulting Negative is therefore soft, and free from violent contrasts of light and shade.

It has been said that the employment of Sulphate of Iron *invariably* shortens the necessary exposure in the Camera, but this statement is incorrect. That it does so in a bad light and at a low temperature is certain, but probably if the experiment be made under opposite conditions, the same result will not be obtained. In the case of a sun-lit view, for instance, taken in the spring months, the Writer finds Pyrogallic Acid abundantly strong enough to bring out the weaker radiations with a minimum of exposure, the Collodion being supposed to contain only Iodides.

Acetate of Iron has been used in Photography: it produces nearly as much density as Pyrogallic Acid, and at the same time is equal to the Sulphate in its power of developing the shadows. A similar effect may be obtained by mixing the ordinary Sulphate of Iron with half its weight of crystallized Acetate of Soda.

However much opinions may be divided as to the relative merits of Pyrogallic Acid and Sulphate of Iron as developers for a simply Iodized Collodion, no doubt exists that the latter is the more suitable for a Bromo-iodized Collodion. The great reducing power of the Salts of Iron is precisely what we require in the presence of Bromide of Silver, a salt which considerably retards reduction; and, as already shown, the fine red or black tone which Pyrogallic Acid imparts to the Negatives is not seen when the Collodion contains Bromide. The tendency to produce fogging which the Salts of Iron exhibit in the case of a simply iodized Collodion, is nearly absent when the Collodion contains Bromide.

Effect of Varying the Mode of Development.—The remarks made in the last Section, on the contrast in Collodion Positives as affected by the mode of development, apply also in the case of Negatives. We have already seen that an ordinary Iodized Collodion may, when employed in the subdued light of a glass studio, produce a soft Negative, and yet in a glare of sunshine it may yield an intense Negative. If the intensity be greater than is desirable, it is in the power of the operator to remedy it in a measure by removing a portion of the free Nitrate of Silver from the surface of the film. To effect this, it will only be necessary to flood the plate with a large quantity of a diluted solution of Pyrogallic Acid containing perhaps half a grain of the reducing agent to the ounce of water: or, more effectually still, to wash the plate with water, after exposure, and then to develope it by the addition of a few drops of the Bath solution to the Pyrogallic Acid. The picture thus obtained will have less contrast and solarization than before, and the developing action may be pushed far enough to bring out the deepest shadows, without adding too much to the intensity of the lights. When the converse of the foregoing happens, and the image on a simply Iodized Collodion is deficient in contrast, it is recommended to increase the relative proportion of Nitrate of Silver, by making an addition of that substance to the developer before applying it to the film.

Fixing Agents for Negatives.—Cyanide of Potassium acts quickly in removing the Iodide of Silver, and the plates do not require much subsequent washing; the film is also left in a favourable state for continuing the development with mixed Pyrogallic Acid and Nitrate of Silver when required. On the whole, however, we recommend Hyposulphite of Soda in preference to the Cyanide of Potassium, as safer in the hands of a beginner. Negative images are more easily dissolved by fixing agents than Collodion Positives, and therefore, unless much care be exercised, the application of Cyanide lowers the intensity materially, and whitens the surface of the picture by converting it into Cyanide of Silver. This is especially the case in working in the open air, and attempting to fix the image whilst the sun is shining upon the plate. Collodion Negatives developed with Sulphate of Iron are less soluble in solution of Cyanide of Potassium than those in which Pyrogallic Acid is used as the reducing agent; and the use of Bromide in the Collodion likewise diminishes the solubility.

Modes of strengthening a finished Impression which is too feeble to be used as a Negative.—The ordinary plan of pushing the development cannot be applied *with advantage* after the picture has been washed and dried. In that case, if it is found to be too feeble to print well, its intensity may be increased by one of the following methods:—

1. *Treatment of the image with Sulphuretted Hydrogen or Hydrosulphate of Ammonia.*—The object is to convert the metallic Silver into *Sulphide of Silver,* and if this could be done, it would be of service. The mere application of an Alkaline Sulphide has however but little effect upon the image, excepting to darken its surface and destroy the Positive appearance by reflected light: the structure of the metallic deposit is too dense to admit of the Sulphur reaching its interior.

This may be obviated by first converting the image into the white Salt of Mercury and Silver by the application of Bichloride of Mercury, and afterwards treating it with solution of Sulphuretted Hydrogen or Hydrosulphate of Ammonia. Negatives produced in this way are of a brown-yellow colour by transmitted light, and remarkably opaque to chemical rays.

The employment of Bichloride of Mercury has one serious drawback, viz. the injurious effect which even a trace of a Salt of Mercury exerts upon the sensitiveness of Iodide of Silver: hence if the glass plates are not cleaned with extraordinary care, or if the slighest portion of the Mercury Salts finds its way into the Bath, injurious effects will follow. The Writer dispenses entirely with the employment of the Bichloride, and acts on the image with a solution of Iodine in Iodide of Potassium until it is converted into Iodide of Silver, after which the Hydrosulphate is applied in the usual way. The Hydrosulphate is in fact the principal agent in producing the intensity, and no other chemical is actually required, excepting for the purpose of rendering the image sufficiently porous to allow of a proper penetration by the Sulphur. Practical directions for carrying out this intensifying process, will be found in Part II. under the head of "Copying Maps and Diagrams."

2. *MM. Barreswil and Davanne's Process.*—The image is converted into Iodide of Silver by treating it with a solution made by dissolving a grain of Iodine in an ounce of water by the aid of a little Alcohol. It is then washed —to remove the excess of Iodine,—exposed to the light, and a portion of the ordinary developing solution, mixed with Nitrate of Silver, poured over it. The changes which ensue are precisely the same as those already described (p. 40); the whole object of the process being to bring the metallic surface back again into the condition of Iodide of Silver modified by light, that the developing action may be commenced afresh, and more Silver deposited from the Nitrate in the usual way.

In a former Edition a solution of Iodine in Iodide of Potassium was recommended for the conversion of the image into Iodide in this intensifying process. This method however is liable to fail, for if the solution be kept upon the plate until the whole image becomes yellow, the sensitiveness to light is in great measure lost. At present therefore the Writer is of opinion that a weak aqueous solution of Iodine is preferable, and that the condition of the film so produced is analogous to that of the Daguerreotype, the metallic Silver being acted on superficially, and never entirely converted into Iodide.

CHAPTER VIII.

ON THE THEORY OF POSITIVE PRINTING.

THE subject of Collodion Negatives having been explained in the previous Chapter, we proceed to show how they may be made to yield an indefinite number of copies with the lights and shadows correct as in nature.

Such copies are termed "Positives," or sometimes "Positive prints," to distinguish them from direct Positives upon Collodion.

There are two distinct modes of obtaining photographic prints;—first, by development, or, as it is termed, *by the Negative process,* in which a layer of Iodide or Chloride of Silver is employed, and the invisible image developed by Gallic Acid; and second, by the direct action of light upon a surface of Chloride of Silver, no developer being used. These processes, involving chemical changes of great delicacy, require a careful explanation.

The action of light upon Chloride of Silver was described in Chapter II. It was shown that a gradual process of darkening took place, the compound being reduced to the condition of a coloured *subsalt;* also, that the perfection of the change was increased by the presence of excess of Nitrate of Silver, and of organic matters, such as Gelatine, Albumen, etc.

We have now to suppose that a sensitive paper has been prepared in this way, and that a Negative having been laid in contact with it, the combination has been exposed to the agency of light for a sufficient length of time.

Upon removing the glass, a Positive representation of the object will be found below, of great beauty and detail. Now if this image were in its nature fixed and permanent, or if there were means of making it so, without injury to the tint, the production of Paper Positives would be a simple department of the Photographic art; for it will be found that with almost any Negative, and with sensitive paper however prepared, the picture will look tolerably well on its first removal from the printing-frame. Immersion in the bath of Hyposulphite of Soda however, which is essentially necessary in order to fix the picture, produces an unfavourable effect upon the tint; decomposing the violet-coloured Subchloride of Silver, and leaving behind a red substance which appears to be united to the fibre of the paper, and, when tested, reacts in the manner of Suboxide of Silver.

Other chemical operations are therefore required to remove the objectional red colour of the print, and hence the consideration of the subject is naturally divided into two parts; first, the means by which the paper is rendered sensitive, and the image impressed upon it;—and secondly, the subsequent fixing and *toning,* as it may be termed, of the proof.

The present Chapter will also include, in an additional Section, a condensed account of the most important facts relating to the properties and the mode of preservation of photographic prints.

SECTION I.

Printing the Proof.

When a sheet of the photographically prepared paper is exposed to the light, we observe it to assume various colours, each one deeper and more intense than that which preceded it. These shades of colour are not always the same, but vary more or less with the mode of preparing the paper, as will presently be shown. The sequence of tints, in the case of a paper prepared simply with Chloride and Nitrate of Silver, is as follows:—Pale violet, violet-blue, slate-blue, bronze or copper-colour. When the bronzed stage is reached, there is no further change.

On immersing the paper darkened as above described, in the fixing bath of Hyposulphite, the violet tones are destroyed, and the print assumes a red or brown colour, which is most intense in the parts where the light has acted longest. Therefore we see, that, to produce a good photographic print, the Negative must possess considerable opacity in the dark parts; for if it be pale and feeble, the light passes rapidly through it and darkens the paper universally, before the exposure has been sufficiently prolonged to ensure the requisite degree of reduction; hence the deepest shadows of the resulting Positive are not dark enough, and there is a want of contrast which is fatal to the effect. A good Negative should be so opaque as to preserve the lights of the printed image beneath clear, *until the darkest shades are about to pass into the bronze or coppery condition.* If the amount of intensity be less than this, the finest effect cannot be obtained.

Let us now pass on to consider more carefully the exact function of each of the constituents of the sensitive sheet, and to show how the effect may be varied by altering their relative proportions, or by introducing substances not usually employed.

The printing process in its most simple form may be conducted as follows:—Take pure Swedish filtering-paper, free from size and other extraneous matters, and float it upon a solution of Nitrate of Silver containing about one hundred grains to the ounce of water: then dry and expose it to a strong sunlight. The darkening action will take place, but with such extreme slowness as at first to convey the impression that the paper is quite insensitive to light; by perseverance, however, for three or four days, a pale-brown tone will be obtained. One cause of this difficulty with the simply Nitrated paper is that the Nitric Acid in the Nitrate of Silver retards the reduction, and the pure fibre of paper does not possess a sufficient affinity for Oxygen to enable it to overcome the opposition. It is possible however to remove the Nitric Acid by adding Ammonia to the Nitrate of Silver, and so to leave the paper in contact with a simple *Oxide* of Silver; this accelerates the change considerably, and a few hours' exposure to strong sunlight will then give the requisite opacity.

Swedish paper, however, although prepared with Ammoniacal Oxide of Silver, darkens very slowly excepting in strong sunlight, and the Photographer will find by experiment that a minute quantity of Chloride of Silver in the prepared paper will enable him to obtain the desired result in *minutes* instead of *hours* of exposure. Even when an insoluble Salt of Silver like the Phosphate or Citrate is substituted for the Chloride, the prepared paper is more sensitive than when consisting of simple vegetable fibre saturated with solution of Oxide of Silver. The part therefore which we assign to such insoluble Salts is that of "accelerators" to the luminous agency, and of all accelerators the Chloride of Silver appears to be the most remarkable.

The following experiment will prove instructive in further exhibiting the function of the Chloride of Silver in ordinary sensitive paper. Take a piece of ordinary bibulous paper and float it for an instant upon the Nitrate of Silver solution which Photographers employ in printing; then blot it off, and immerse for five minutes in a solution of common salt containing ten grains to the ounce. This paper when freed from excess of salt by washing in distilled water, may be viewed as containing only Chloride of Silver in contact with the Cellulose. On exposing it to the light it will be found to change rather quickly to a pale violet tone. At that point, however, the reducing action will be suspended, and when the fixing bath of Hyposulphite of Soda is brought to bear upon the image, it will nearly disappear in consequence of decomposition and solution. Pictures printed upon Chloride of Silver only would be altogether wanting in contrast, consisting only of half-tints, without any depth of shadow.

In a second experiment, take several strips of paper prepared as described for experiment No. 1, and apply washes of Nitrate of Silver of various degrees of concentration, such as 5, 10, 20, 40, 80, and 100 grains to the ounce of water. On drying the strips, and exposing them successively beneath the same Negative matrix, it will be found that the pictures become more and more vigorous in proportion as the Nitrate of Silver solution increases in strength, but that beyond a certain point a further increase in the concentration of the Nitrate of Silver does not add to the effect.

Having performed the above experiments, we are prepared to conclude therefrom,—that the office of the free Nitrate of Silver is to furnish the material which composes the metallic part of the image, and so to give *intensity;* the Chloride meanwhile accelerating the change and adding to the *sensitiveness* of the prepared paper.

It remains now to consider the action of the organic supporting basis, and this is perhaps equally important with that of the other constituents, although in the present state of our knowledge it cannot be defined with the same precision. If we take a sheet of Swedish filtering-paper and immerse it in cold Nitro-Sulphuric Acid, in such a way as to wet only one half of the paper, the surface after washing and drying will consist in part of Cellulose and in part of Pyroxyline. Now it has already been shown (p. 24) that Pyroxyline is in a manner indifferent to the Salts of Silver, and that Chloride of Silver, supported by Pyroxyline, behaves in the sun's ray much in the same manner as Chloride of Silver supported upon a glass plate: hence we should anticipate that if a sheet of paper were converted only partially into Pyroxyline, and subsequently treated with Salt and Nitrate of Silver, the two halves would behave differently on exposure. This expectation is correct, and the experiment will show not only that the darkening is more decided upon the unaffected Cellulose, but that the image is less dissolved by the fixing bath, and has a softer and more velvety shade of colour. In the one case the fixed print is of a warm red, and tones in solution of Chloride of Gold to a fine purple-black; in the other, it is very faint and metallic, or, if examined after toning, cold and slaty in aspect.

We may therefore add to what we have before said, the following statement, viz. that whereas the function of the Chloride is to impart sensitiveness in Photographic printing, and that of the Nitrate of Silver to give intensity, the Organic Matter acts by brightening the *colour.* The artist requires an image which after simply fixing shall be of a *warm red tone,* and thus be capable of yielding a full brown or black on subsequent treatment with the Gold solution; he will find by experience that organic compounds of Silver in the paper, produced by adding Albumen or similar substances to the salting bath, will afford him the means of obtaining these varied tones, and that without them the picture will lack richness of effect.

The chemist may perhaps be disposed to inquire more particularly how the organic substance acts; but we must be guarded in answering this question, because it involves the consideration of a class of actions which belong to an obscure Chapter of Chemistry. It is known that many oxides and subsalts of metals, attach themselves in a peculiar way to animal and vegetable fibre, although the precise nature of the union is uncertain. These same Oxides commonly exhibit an affinity for the colouring matters used in dyeing, and are known as "Mordants," because they bind the colours on to the cloth and fix them so that they resist the action of water. An ordinary "iron mould" is a familiar instance of this kind of action, the red stain upon the linen consisting of an Oxide or Subsalt of Iron, adhering to the fibre. Organic substances saturated with Bichromate of Potash and exposed to light, furnish another example, for it has been shown that the Bichromate becomes in such a case reduced to an Oxide of Chromium, which is a true mordant, although a feeble one. Now in the process of Photographic printing we suppose that a Protoxide of Silver is reduced to the state of a lower or *sub*-oxide, and that this suboxide combines with the Cellulose. Further, the fact of the Cellulose or other organic matter having an affinity for a suboxide facilitates the formation of that substance, and enables it when formed to withstand the action of bodies like Hyposulphite of Soda, which are known to possess the property of decomposing Suboxide of Silver when existing in an uncombined state.

If Photographic printing can be shown to bear any analogy to the operations employed in the art of dyeing, it would be anticipated that certain kinds of fibre would exhibit the affinity for the mordant oxide more completely than others. It is well known, for instance, that woollen stuffs take certain dyes with more facility than materials made of linen or cotton, so that if a cloth be woven partly of wool and partly of cotton, a colour may be fast upon the former but removable by washing from the latter. So in Photography we find that cotton immersed in Nitrate of Silver is less readily affected by the sun's rays than wool or silk. In speaking of the use of animal substances in printing we must not indeed lose sight of the fact that these tissues invariably contain traces of Chloride and also of Phosphate. The pure animal fibre, however, is believed to play an important part in the process, quite independently of any inorganic salts. This action of the animal matters we now proceed to consider further.

Swedish paper prepared with Chloride and Nitrate of Silver, although sufficiently sensitive, could not be used in Photography. The picture would exhibit a complete want of definition, and would also appear to be sunk in the substance of the paper so as to be seen more distinctly by transmitted than by reflected light. If the Salt were employed in anything like quantity, Chloride of Silver would form in loose flakes upon the surface, and would burst out and fall away into the Bath. The *sizing* of Photographic paper has undoubtedly a mechanical action, keeping the chemicals upon the surface, and thus securing an even layer of Chloride of Silver in a state of excessive division. This however, as already shown, is not the sole use of the sizing, for when it consists of Albumen or Gelatine it communicates a fine red tint to the image, and gives what artists term an aspect of transparency to the whole picture.

If we examine the action of the animal sizing chemically, we find that Albumen, Caseine, and Gelatine, all withdraw from the Bath large quantities of Nitrate of Silver, so that the solution becomes continually weaker. A sheet of transparent Gelatine, allowed to swell up by imbibing a solution of Nitrate of Silver, of the strength of twenty grains to the ounce of Water, will appropriate nearly the whole of the dissolved Nitrate, so that the liquid expelled from it by squeezing will yield less than three grains of Silver to the ounce. The Gelatine forms with the Nitrate of Silver a compound which may be designated Gelatino-Nitrate of Silver, and which is highly photographic and colorific. Chloride of Silver thrown down in presence of this Gelatino-Nitrate, does not clot together in the same manner as the pure Chloride of Silver, but exists in a state of excessive division, and remains for a long time without subsiding to the bottom of the liquid. Exposed to light the Gelatino-Nitrate of Silver darkens to a ruby-red colour; and Chloride of Silver precipitated from an aqueous solution of the Gelatino-Nitrate never assumes, in the sun's rays, the slate blue colour characteristic of Subchloride of Silver, but changes quickly to a chocolate-brown tone. In the case of a paper sized with Albumen or Gelatine, and subsequently salted and rendered sensitive, the action of the light is evidently compound, for the Chloride decomposes at the same time that the Oxide of Silver is reduced by the animal matter. The behaviour of the darkened paper always varies with the proportion which the Chloride bears to the organic substance: when the former is relatively large, the print exhibits the violet shades on its removal from the frame, and dissolves considerably in the fixing bath; but with the organic matters in excess, the colour of the print is brick-red from the very first, and the tones are less affected by the solvent action of the Hyposulphite of Soda.

FURTHER OBSERVATIONS ON THE PRINTING OF PHOTOGRAPHIC PROOFS.

In considering the process of positive printing more carefully we may divide it as follows:—the paper; salting bath; sensitizing solution; various kinds of organic matter.

The Paper.—The quality of paper sold for Photographic purposes is variable and often inferior: the following is all that the Writer has been able to collect upon the subject:—

A difference exists in the length and thickness of the fibre of various kinds of Cellulose, so that the resulting paper may be either coarse or smooth grained. Linen rags are esteemed superior to Cotton rags, and new Linen is better than old. A paper sold in the market as Towgood's Paper has in the hands of the Writer given finer definition and absence of grain than any other kind: hence this paper is well adapted for Stereoscopic pictures to be viewed through a magnifying lens: some of the foreign papers are so coarse, that the structure is at once seen on placing the print in the instrument, and no amount of Albumen will conceal this defect. The smoothness of a Photographic paper cannot be estimated until the print has passed through all the processes of fixing and washing, because by hotpressing and other appliances it is easy to get up a fictitious glaze.

Supposing the paper to be properly made, in the first instance, yet much will depend upon the perfection of the process adopted for sizing. The defects which occur in a paper badly sized are of the following kind. First, portions of the finished pictures are pale in colour and have a spotty appearance, due to an inequality in the imbibition of liquid by the paper; some parts of which being comparatively impermeable by the Nitrate of Silver, and others more porous, the surface is unequally sensitive and darkens in an irregular manner. Secondly, when the sizing is very soft the chemicals sink too deeply into the paper, and the proofs are what is termed *mealy*, and ineffective. Albumen, even when employed without any addition of water, gives very little glaze upon a paper of this kind, and no surface vigour can be obtained: the sheets are often very tender, so that they become torn in the many washings to which the photographic proofs are necessarily subjected; and when Albumen is used, there is a strong tendency to a superficial *blistering* in the fixing bath, or in the washing waters, inasmuch as the Alkaline solutions used in toning tend to lessen the tenacity of the size. Thirdly, paper may be too strongly sized, and when such is the case, the amount of gloss given by Albumen is considerable, but the prints are not easily toned in the Gold solutions, and are fixed with difficulty.

There are two principal modes of sizing paper: first, with a mixture of Starch and Resin partially saponified by an Alkali, and second, with Gelatine hardened by Alum. The first method is principally practised on the Continent, and the latter in the papers of home manufacture. Papers sized with Starch and saponified Resin have necessarily an *alkaline* reaction, whilst the Gelatine sized papers exhibit an acidity due to the Alum. In each case the paper improves more or less by keeping, because the size becomes gradually harder, and the sheets are in consequence less easily torn in the washings. Opinions are divided as to which mode of sizing is to be preferred, but the general impression is that the Starch offers more mechanical advantages when Albumen is to be used in the salting solution, whereas the Gelatine size gives a better surface layer of Chloride of Silver in the case of plain salted paper prepared without Albumen. The French firm of Canson Brothers have a mode of preparing a Starch-sized paper which stands the action of hot water remarkably well: such a paper may be made into a tray and filled with warm water without the liquid percolating through: an English paper sized with Gelatine would imbibe hot water rapidly, and would swell in consequence. The Canson paper however is rather defective upon the surface, and gives less gloss with Albumen than an English paper. Papier Rive is also a Starch-sized paper, but frequently the sizing is too soft. The colour of the finished Albumen picture is remarkably good on this latter paper, but no precise information can be given, inasmuch as the composition of the size is unknown.

The Photographic properties of the paper are much affected by the mode of sizing adopted, even when Albumen is afterwards used, for the picture is probably formed partly upon the Albumen, and partly in the sizing. English papers tend to give red tones which become brown or chocolate-coloured in the finished print. This is due in part to the use of Gelatine, which, as before shown, forms a compound with Nitrate of Silver, darkening in the sun to a ruby-red colour; but in part to the Alum employed to harden the Gelatine, since Alum is an acid salt, and acids tend to impart a foxy-red tone to the image. The foreign papers sized with Starch or Resin, produce tones which are of a sepia-brown after fixing, and of a purple-black when treated with the Solution of Gold; the reason is partly because the Starch and Resin do not, like Gelatine, exert a very marked action in reddening the picture, and partly because the sizing has an alkaline reaction, and alkalies are found to diminish redness, just as acids increase redness.

Many additional observations might be made on the colour of the image yielded by the various commercial qualities of Photographic paper, but the above general division into Gelatine-sized paper, and Starch-sized paper, will be sufficient. At the same time it should be borne in mind that the manufacturer has it in his power, by adding small quantities of organic bodies to the size, to modify the tone given by the paper, even when employed in the albuminized state. Hence although the general characters of a paper may be those of a Starch-sized paper, yet the print may assume a brick-red colour in place of a violet tone, in consequence of some addition made to the size.

Rendering the Paper Sensitive.—Under this head we speak first of the salting solution, and second of the Nitrate Bath. Observe in the first place that the strength of both solutions should be properly adjusted, so that when the amount of Chloride of Silver in the paper increases, the excess of free Nitrate of Silver may increase also. Theoretically three parts by weight of Nitrate of Silver will precipitate nearly one part by weight of Salt, and a slight excess of the Nitrate of Silver will remain. These proportions however are not always adhered to, because in Photographic printing there are many disturbing conditions. The sizing of the paper, and the Albumen glaze, appropriate a quantity of free Nitrate of Silver as already shown (p. 179); and not only so, but the proportions of Nitrate and of Chloride left in the paper, vary with the method of applying the solutions. There are three modes of spreading solutions on photographic paper,—by brushing, by floating, and by total immersion. The first leaves a small, and the third a large amount of solid matter upon the paper, whilst the second gives a variable result according to the length of time the paper is left floating upon the Bath. Experience shows that for an Albuminized paper, both solutions being applied by floating, the Nitrate Bath should be about six times as strong as the Salting Bath, and should be left twice as long in contact with the paper. In the case of a paper *floated* upon the salting bath, and *brushed* with the Nitrate of Silver, the latter may be twelve times stronger than the former; and when the papers are salted by total immersion, and sensitized by brushing, the Salt may conveniently be reduced to a fifth of the ordinary weight, and the Nitrate of Silver left as before, so that the proportions may be nearly as thirty of Nitrate to one of Salt.

The strength of the Nitrate Bath in Photographic printing must also be regulated partly by the mode of sizing adopted. A hard-sized English paper keeps all the chemicals comparatively upon the surface, and does not require such concentrated solutions as a paper which is more soft and spongy. Also when any organic matter like Gelatine or Albumen is added to the salting bath, the amount of Salt must be lessened, because the glutinous character of such fluids causes more to be retained upon the surface of the paper. The difference in the atomic weights of the various soluble Chlorides used in salting must also be borne in mind; ten grains of Chloride of Ammonium contain as much Chlorine as eleven grains of Chloride of Sodium, or as twenty-two grains of Chloride of Barium (see the Vocabulary, Part III.).

The Salting Bath.—The foregoing remarks apply both to the Saline and to the Sensitizing bath; in those which follow, the two will be considered separately. The sensibility of Photographic paper is regulated up to a certain point by the amount of salt used in its preparation. The quantity of alkaline Chloride determines the amount of Chloride of Silver; and with a proper excess of Nitrate of Silver, papers are, up to a certain point, more sensitive in proportion as they contain more of the Chloride. Highly sensitized papers darken rapidly, and pass very completely into the bronze stage. Those containing less Chloride darken more slowly, and do not become bronzed with the same intensity of light. A Photographic print formed upon a paper highly salted and sensitized, is usually vigorous, with great contrast of light and shade; particularly so when the printing is conducted in a strong light. Hence it will be an advantage, with a feeble Negative, and in dull weather, to double the ordinary quantity of Salt; whereas in the case of an intense Negative, and with direct sunlight, the deep shadows will be too much bronzed unless the quantity of

Chloride of Silver in the paper is kept low, so as to stop the action of the strong lights at a certain point, and thus to allow the feeble rays time to come forward.

With regard to the effect which the amount of Chloride in the paper exerts upon the colour and general appearance of the print, the following statements may be made:—Highly salted and sensitized papers give a picture more nearly approaching to black, than those which, containing a small proportion of Chloride of Silver, are less sensitive to light. Hence in printing upon paper weakly sensitized, in order to bring out the finer details of a highly intense Negative, we find the image unusually red after fixing, and of a brown or mulberry colour when toned.

It is possible to carry the proportion of Salt too far in Photographic printing; in that case, even though the excess of Nitrate be properly maintained, the print appears cold and dull, because the Chloride of Silver is in too large quantity with reference to the organic matter. A reduction in the amount of Salt on the other hand, simply leaves the image of less contrast but does not destroy its velvety softness: transparency and warmth depending upon the organic matter, and not upon the Chloride.

The Nitrate Bath.—The compound on which a positive print is formed is a Chloride, or an organic Salt of Silver, with an excess of Nitrate of Silver: hence nothing is gained by increasing the proportion of Chloride of Sodium, unless at the same time an addition be made to the quantity of free Nitrate in the sensitizing bath.

Let us consider more minutely the appearances which present themselves when the Nitrate Bath is too weak. If a sample of the ordinary salted and albuminized paper be floated for two or three minutes upon a solution of Nitrate of Silver of the strength of twenty grains to the ounce of water, the quantity of Nitrate left upon the surface will be insufficient, and the following defects will appear:—The paper darkens on exposure but it does not reach the bronzed stage, the action appearing to stop at a certain point. On placing the print in Hyposulphite of Soda it becomes very pale, and when tinted looks cold and slaty, without depth of shadow. In almost all cases there exist on pictures of this kind large spots or patches of a paler colour than the surrounding parts, since the capillarity of the paper is unequal and some portions absorb slowly. The spots are most abundant at that edge of the paper which is uppermost in drying, and are nearly absent at the lower part where the excess of liquid drains down and becomes concentrated by evaporation. In a second experiment the salted paper may be left as long as ten or fifteen minutes upon the same weak Bath: the result will be improved thereby, for the Albumen is allowed time to draw to itself more of the Nitrate of Silver. A third experiment may consist in dissolving forty grains of Nitrate of Silver in an ounce of water, and floating portions of the same paper upon it: the shadows will be deeper than before, and the colour warmer, but in all probability there will be room for further improvement, since a forty-grain Bath is scarcely strong enough for the foreign papers albuminized with a ten-grain Salt solution, although sufficiently so for the English albuminized paper of the same strength. Lastly, dissolve sixty grains, eighty grains, and a hundred grains of Nitrate of Silver in three separate ounces of water and float upon each, when it will be found that the pictures are all good, and differ very little in appearance. If, however, the time of floating be reduced to a single minute, the Nitrate Bath of a hundred grains will prove the best; and some artists consider that, in Photographic printing, both time and money are saved by employing a highly concentrated Nitrate Bath and floating the papers upon it for not more than a minute. The defect which the Writer would apprehend under such circumstances would be a tendency to spottiness from uneven absorption by the paper, since a lengthened floating is certainly favourable to even precipitation of the Chloride.

Those precautions which are observed in making the Nitrate Bath for Collodion Negative Photography, are unnecessary in the case of the Bath for printing. We saturate the former Bath with Iodide of Silver, but the printing Bath need not be saturated with Chloride of Silver, since this compound, although not absolutely insoluble in solution of the Nitrate, dissolves in a proportion so small, that it may be disregarded. Neither is it actually necessary to examine the crystals of Nitrate of Silver for free Nitric Acid, for unless the sample of Nitrate be very impure, the retarding effect of the Nitric Acid will be inappreciable, and especially so in the case of albuminized paper, which possesses usually a slightly alkaline reaction.

A Nitrate Bath containing free Oxide of Silver, however, and giving an alkaline reaction to Litmus, would in some cases be injurious, since Alkaline Nitrate of Silver does not properly coagulate *Albumen*, and in consequence a Bath of this kind soon exhibits a white turbidity when the papers are floated upon it. There are certain qualities of albuminized paper sold in commerce, which tend to precipitate the same white substance in the sensitizing Bath, and the Writer believes this to be due in part to alkalinity. The *strength* of the Bath, however, must always be noted; for the weaker it becomes, the greater the tendency to dissolve away the Albumen without coagulating it. In such a case the greater part of the Nitrate of Silver is converted into Chloride, and not being properly retained upon the surface of the paper by the coagulated Albumen, falls away into the solution.

Papers rendered sensitive upon a Nitrate Bath faintly acid with Nitric Acid, or with Acetic Acid, are less liable to spontaneous reduction in the dark: whereas papers prepared upon a Bath which has become alkaline from continued employment of an alkaline albuminized paper, or other causes, soon change on keeping.

Acetate of Silver exercises an important effect in the Photographic Negative Bath, but in the Bath for printing, its action is not very remarkable. The only perceivable difference is a little extra bronzing in the shadows, and an increased difficulty of keeping the paper without discoloration in the dark. *Organic matter* is also mentioned as greatly influencing the action of the Negative Nitrate Bath, but in the printing Bath its effect is inappreciable, and even when the Bath has become highly coloured by the Albumen, its action is nearly the same as at first. The brown coloration above alluded to is probably due to the gradual formation of a *Sub*-Albuminate of Silver, partially soluble in solution of Nitrate of Silver.

Before leaving this subject we must advert for a moment to the employment of the compound known as Ammonio-Nitrate of Silver* in Photography. This compound may be viewed as a solution of *Oxide* of Silver, in place of the usual solution of *Nitrate* of Silver; for by dropping Ammonia into the Bath, the Nitric Acid is combined with Ammonia, and the Oxide of Silver is consequently left in a free state. The first advantage derived from the use of the Ammonio-Nitrate of Silver is an increase of sensitiveness, and also of intensity in the image. This will be understood if we remember that the action of light in producing the print is of a *reducing* nature. Hence the substitution of Oxide of Silver for Nitrate of Silver facilitates the decomposition; just as Ammonio-Nitrate of Silver is more readily reduced by Gallic or Pyrogallic Acid than the simple Nitrate (see p. 32). Another advantage of the Ammonio-Nitrate is that the colour of the print is improved, the redness being diminished and a soft velvety aspect being given to the image such as would be difficult to secure, on plain paper, with simple Nitrate of Silver.

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* The Chemistry of Ammonio-Nitrate of Silver is explained in the Vocabulary, Part III.

There are, however, disadvantages attending the use of Ammonio-Nitrate of Silver, which prevent it from being generally adopted. In the first place it does not coagulate Albumen, so that albuminized paper floated upon Ammonio-Nitrate of Silver loses its surface-varnish, and appears *dead*, like the plain paper. Secondly, it is more liable to spontaneous change, and to discoloration by traces of organic matter, than simple Nitrate of Silver; and hence when used as a Bath, it becomes perfectly black in the course of a few days, from sizing, etc., dissolved out of the salted paper. Thirdly, the action of the salted paper upon Ammonio-Nitrate of Silver liberates *free Ammonia*, as will be seen by referring to the Vocabulary, Part III., and this free Ammonia being a solvent of Chloride of Silver, attacks the sensitive coating and dissolves it, thus producing white lines and transparent markings. The latter objection is the most formidable of all, and in consequence of it the Ammonio-Nitrate has nearly fallen into disuse, excepting in the case of papers purposely prepared with a very small quantity of salt, so as to avoid the production of free Ammonia as far as is possible. Such papers are economical, because a comparatively weak Silver solution suffices to sensitize them, and to give the requisite vigour to the shadows. The colour of the finished picture, however, on Ammonio-Nitrate paper feebly salted, is not black, but rather of a chocolate-brown, since the diminution in the quantity of Chloride increases redness, and the effect of the Ammonio-Nitrate of Silver in an opposite direction is not sufficient to counteract this tendency.

Organic Bodies used in Printing.—The most important of these is Albumen. Albumen is remarkable for producing a smooth and homogeneous layer upon the very surface of the paper, so that every detail of the Negative is rendered with an amount of distinctness which cannot be obtained in any other way. The prints are clear and brilliant, retaining even when dry much of the transparency which plain paper pictures exhibit only whilst in the water.

The main obstacle to the general adoption of Albumen is the difficulty of applying it evenly to the surface of the paper. Being a glutinous fluid, and not immediately amalgamating with the sizing, it is apt to run into lines when the paper is floated only for a short time, such as a few seconds; whilst on the other hand, if the paper be left for several minutes upon the Albumen, a portion of the size is dissolved, and the Albumen in consequence sinks into the paper, and does not impart the proper amount of gloss. In order to understand this we must bear in mind that Albumen is not a neutral fluid, but possesses an alkaline reaction, due to the presence of small quantities of alkaline Phosphate, etc.; hence on adding Chloride of Ammonium to Albumen a development of free Ammonia takes place, easily perceptible to the smell, and Ammonia is a solvent of the materials used in sizing paper. To overcome this difficulty of applying the Albumen, and to obtain a greater amount of gloss, makers of albuminized paper have found it advantageous to expose the Albumen in an open vessel to the air, until a considerable amount of evaporation has taken place. This evaporation does not always render the Albumen more glairy; on the other hand, the fluid often becomes gradually more limpid, acquiring a rather offensive odour, and an *acid* reaction to Litmus paper. Albumen so prepared runs upon the paper very easily, and does not dissolve the size, but it possesses some objectionable qualities, to be pointed out under the head of "Toning." That defects should arise from decomposition of Albumen, is not to be wondered at when we consider that one of the constituents of this substance is *Sulphur*, which during the putrefaction passes into the state of Sulphuretted Hydrogen, and is the cause of the offensive smell. The Nitrate Bath is soon rendered turbid by the use of stale albuminized paper, and the sensitiveness to light is injured, so that the half-tones of the picture do not appear until after a prolonged exposure. In preparing a highly albuminized paper the requisite amount of evaporation may be effected over hot water at a temperature short of the coagulating point of Albumen; or what in most cases will be found sufficient, the wet Albuminized sheet may be rapidly dried by an ascending current of hot air. Pressing between heated rollers will still further condense the finished sheet, and give it the appearance of possessing a hard and glossy surface.

The reddening action of Gelatine, although greater than that of Starch, is less than that produced by Albumen, and the surface brilliancy is also less. Caseine, the animal principle of Milk, gives good definition, and a red colour like Albumen, but is destitute of gloss. Were it not for the difficulty of preparing soluble Caseine, it would probably come into more extended use, since the tone, when modified by a deposit of Gold, is very agreeable. Serum of Milk is a convenient form of employing a dilute solution of Caseine; since the rennet used in coagulating the milk does not separate the whole of the Caseine, but leaves a little dissolved in the liquid: by agitation with white of eggs, and subsequently boiling, the suspended oil-globules may be entangled, and the Serum thus clarified.

Citrate and Tartrate dissolved in the Salting Bath exercise an effect upon the colour of the print quite as remarkable as that of Albumen. Paper prepared with Citrate, in addition to Chloride of Silver, darkens to a fine purple colour, which becomes brick-red in the fixing bath. Oxalate, however, has not the same action; paper prepared with Oxalate and Chloride of Silver darkening to a violet-blue colour, resembling that of the ordinary Subchloride. These facts will enable the reader to understand the remarks previously made on the composition of materials for sizing paper (p. 182); and to see that the maker might, if so desired, introduce small quantities of organic substances capable of modifying the colour and general aspect of the print.

Amount of Silver in Sensitive Sheets.—To determine this point roughly, fifty whole sheets of Saxe paper, 18 × 22, albuminized with nearly pure Albumen, containing ten grains of Salt to the ounce, were floated for three or four minutes each, on a fifty-five-grain Nitrate Bath measuring 137 ounces. The sheets were found to remove 17 ounces of liquid from the Bath, and to impoverish the remainder to the extent of five grains of Nitrate of Silver per ounce. The whole quantity of Nitrate of Silver left in each sheet must therefore have been about half a drachm. In a second experiment a quarter sheet of albuminized Papier Saxe was dried and weighed; it was then floated for four minutes upon a forty-five grain solution of Nitrate of Silver, dried and weighed a second time: the gain in weight amounted to seven grains.

Preservation of Sensitive Sheets.—The discoloration of Sensitive Paper in the dark is due to a slow reducing action of organic matter upon the free Nitrate of Silver. The rapidity of the change varies much with the nature of the organic matter, but more so with the state of the Nitrate of Silver. Alkalies in the size of the papers or in the sensitizing bath, facilitate the discoloration, whilst free acid and acid salts, like Alum, etc., retard it: hence French papers darken more quickly than English papers as a rule, and Ammonio-Nitrate paper is more unstable than that prepared with simple Nitrate of Silver.

The comparative dryness of the atmosphere in which the papers are kept, is the principal cause affecting their rate of change, since moisture appears essential to the reduction. Hence the various contrivances devised for drying the paper, the best of which appears to be that of Mr. Spiller, in which a box is constructed with a false bottom pierced by holes, and lumps of quick-lime are placed beneath. To all such plans, however, there are some objections, for it has been said that the papers when rendered absolutely dry do not darken vigorously in the light, and that it is necessary in consequence to leave them for a short time in close proximity to a damp cloth, until the requisite amount of water has been absorbed. Others, again, have observed that although Sensitive Papers, kept for many months in a drying Box, print to a sufficiently deep shade, yet that the image does not tone in the alkaline Gold Bath so readily as a print upon newly sensitized paper.

SECTION II.

Toning the Proof.

By the term "toning" we understand the removal of the reddish colour described in the first Section as the proper tint of a Photographic Positive, after the compounds of Silver unacted upon by light have been extracted by an appropriate fixing bath. Colours approaching to brick-red are in themselves so unartistic that from the very first discovery of Photography means were tried of removing them; and the employment of *Sulphur* was the plan originally adopted for that purpose.

TONING BY SULPHUR.

It is well known that articles of Silver plate become darkened by exposure to the fumes of Sulphur, or to those of Sulphuretted Hydrogen of which minute traces are always present in the atmosphere. If the stopper of a bottle of Sulphuretted Hydrogen water be removed, and a simply fixed Photographic Positive suspended over it, the picture will lose its characteristic red tone and become nearly black. The black colour is even more intense than an experienced chemist would have anticipated, because analysis teaches us that the actual quantity of Silver present in a Photographic picture on paper is infinitesimally small, and it is well known that Sulphide of Silver, although of a deep brown colour, approaching to black, when in mass, exhibits a pale-yellow tint in thin layers, so that a mere film of Silver converted into Sulphide possesses very little depth of colour. To explain the difficulty it has been suggested that the toning action of Sulphur on a red print is probably due to the production of a *Sub*-Sulphide possessing an intense colorific power, like the Sub-Oxide and Sub-Chloride of Silver. When the toned picture is subjected to the further action of Sulphur, it is converted into the ordinary Protosulphide of Silver, and becomes yellow and faded.

It is not necessary to enter into any details of the various processes originally recommended for toning prints by means of Sulphur. The principle was the same in all, but the mode in which the Sulphur was set free and brought to bear upon the proof varied. Commonly, a solution of Hyposulphite of Soda was mixed with some chemical which gradually decomposed it. Everything requiring explanation under this head will be treated in the following Section, when we speak of the properties of the Hyposulphite fixing Bath.

TONING BY GOLD.

After the Sulphur toning process had been discarded, the Salts of Gold were used for improving the normal colour of the Paper Photograph, and the merit of first introducing them is due to M. le Grey, of Paris. These methods being still in vogue will require a detailed description.

The single fixing and toning Bath.—A simple mode and one even now largely followed, is to add Chloride of Gold to the ordinary fixing bath of Hyposulphite of Soda. The prints are immersed in the resulting liquid immediately on taking them from the frame, and the first action of the "fixing and toning bath" is to dissolve out the unchanged Silver salts, and to leave the image of the usual red colour. Shortly however the red colour begins to pass gradually into blue or black and the toning is complete.

At first sight the above process appeared correct both as regards theory and practice. A more extended experience however led to its condemnation, for it was found that the improvement of the colour was not due to a simple precipitation of Gold upon the surface of the image as had been at first supposed, but partly to a deposit of Gold and partly to a communication of Sulphur. When a solution of Chloride of Gold is added to Hyposulphite of Soda, we have in the liquid not only the double Hyposulphite of Gold and Soda known by the name of Sel d'Or, but also a portion of the unstable Tetrathionate of Gold, prone to liberate Sulphur. The action of the Bath is therefore complex from the very first, but becomes more so on keeping the solution for a time, since spontaneous decomposition ensues, as will be more fully shown in the next Section. Practical Photographers were not slow in discovering that the fixing and toning Bath was inconstant in its action, and that although the prints were coloured with as much rapidity in an old as in a newly mixed Bath, yet that the tints were more fugitive in the former case than in the latter. The reason was that whereas the newly-prepared

Bath, acted mostly by depositing Gold, and only partially by communication of Sulphur, the old Bath, on the other hand, toned the prints entirely by Sulphuration. The reader will doubtless be surprised to hear that the colours produced upon the Photographic picture by means of Gold closely resemble those obtained by Sulphur; yet such is the case, for although shades of *blue* are characteristic of Gold, and shades of *brown* of Sulphur, yet it requires a practised eye to distinguish between them, and prints toned by Sulphur often possess the fine purple-black which many suppose to be due to a deposit of Gold.

In the Gold toning process, as now employed, all danger of Sulphurizing the prints is avoided. Hyposulphite of Soda having been proved to suffer decomposition in presence of Chloride of Gold, we no longer mix the two solutions, but prefer to tone the picture first, and fix it subsequently. The colouring action of a simple solution of Chloride of Gold upon the Photographic image may be thus explained:—The Chlorine previously in combination with Gold passes to the reduced Silver salt, bleaching the lighter shades by converting them into the white Protochloride of Silver, and imparting to the shadows a deep violet tint due to the production of Subchloride of Silver; at the same time metallic Gold is deposited, but its effect is not very clearly seen at this stage of the process, since a deep violet colour of nearly equal intensity may be obtained by using a solution of *Chlorine* in place of Chloride of Gold. If however the toned proof be acted upon by a fixing bath of Hyposulphite of Soda, all that portion of the violet colour which depends upon Subchloride of Silver will be destroyed, since the Subchloride is decomposed by fixing agents. Another portion of the colour will resist the action of the Hyposulphite, and this is probably Metallic Gold.

During the whole process of toning in solution of Chloride of Gold we observe a gradual lowering of intensity in the image, in consequence of the biting action of the Chlorine upon the Silver. It has been found that this destructive effect is greater when the solution of the Chloride contains free Hydrochloric Acid, and that it is lessened by the addition of an alkali: hence the employment of *alkaline* solutions of Chloride of Gold, first introduced in this country by Mr. Waterhouse, of Halifax, must be deemed an improvement.

The question as to the manner in which the alkali acts in preventing the image from being eaten away has been variously answered. The first effect of adding Carbonate of Soda to Chloride of Gold is to neutralize the free Hydrochloric Acid which that compound invariably contains, and thus to produce a double Chloride of Gold and Sodium. Now it has been suggested that this Chloride of Gold and Sodium is the real toning agent;—that the process consists essentially in the substitution of Gold for Silver, and that a double Chloride of Gold and Sodium becomes a double Chloride of *Silver* and Sodium, Metallic Gold being at the same time thrown down, and taking the place of the Silver of the proof. Further, it has been urged that in the alkaline toning process lies the real key to the production of permanent Photographic pictures, since the image of Silver, proved to be unstable, is by it converted into an image of Gold, not prone to change. These views are ingenious, but it is doubtful whether they express the truth; for on subjecting the image to the action of Chloride of Gold, we do not find that an atom of Silver is dissolved for each atom of Gold deposited, whilst as regards the entire conversion of the image into Metallic Gold, it may be shown to be impracticable. MM. Davanne and Girard have suggested that the alkaline addition to the Chloride of Gold is useful in neutralizing traces of free Nitric Acid, always liberated when the organic matter reduces the Nitrate of Silver in the process of printing. Undoubtedly the Positive, on its removal from the printing-frame, has an acid reaction, and the Carbonate of Soda in the toning bath must operate beneficially in neutralizing it. This, however, is not the sole use of the alkali, according to the Writer's experience: it probably acts also by converting a portion of the Chloride of Gold into an Oxide of Gold, which is an unstable substance, and may be made to yield up Metallic Gold to the proof.

The following equation shows the general nature of the change which ensues when alkalies or alkaline Carbonates are added to Chloride of Gold:—

$$\begin{aligned}&\text{Chloride Gold} + \text{Oxide Sodium}\\ &= \text{Oxide Gold} \quad + \text{Chloride Sodium.}\end{aligned}$$

This Oxide of Gold is known also as Auric Acid, and is capable of uniting with excess of Alkali, forming a colourless solution. When Carbonate of Soda is added to Chloride of Gold the change into Oxide is at first only partial, and an Oxychloride of Gold is probably formed. The Oxide of Gold, or Auric Acid, does not appear of itself to possess the power of toning the picture; and hence the *total conversion* of the Chloride under the influence of the alkali renders the Bath useless to the photographer. If however a portion of the Gold still remains in the form of Chloride, and the toning action can once be started, a spontaneous decomposition of the Oxide of Gold will take place by catalysis, and a larger quantity of Gold will thus be thrown down without the same injury to the print from communication of Chlorine. These views may appear complex, but they have been adopted by the Author after a careful study of the properties of the alkaline Aurates.

The alkaline substance usually employed for admixture with Chloride of Gold is the Carbonate of Soda, but it has been shown by Mr. Maxwell Lyte that an alkaline Phosphate or Borate produces the same effect. Others again have used an *Acetate*, and it will probably be found that any salt in which the alkaline constituent is only imperfectly neutralized will answer the purpose. In such cases the solution of the Chloride of Gold gradually becomes colourless by an interchange of elements, as above described.

CONDITIONS WHICH AFFECT THE ACTION OF THE ALKALINE GOLD TONING BATH.

a. *Degree of Concentration of the Bath.*—The exact amount of dilution with water in the alkaline toning bath is not of much consequence. A strong bath acts quickly, but is more liable to destroy the middle tints than a weaker solution left upon the image for a longer time. The proportion of Carbonate of Soda is also of minor importance, but it is desirable to use the minimum quantity, since a highly alkaline liquid dissolves the size of the paper, and causes a blistering of the Albumen when the picture is laid in the fixing bath.

b. *The length of time after mixing.*—The two solutions of Chloride of Gold and Carbonate of Soda may be kept separately for any length of time, but on mixing them a chemical change ensues, and the liquid gradually loses its yellow colour. When the solution has become nearly colourless it is in the best state for use, and will remain so for many hours, but after a longer keeping of days or weeks it loses its activity, and deposits Gold in the metallic state on the sides of the bottle: alkaline solutions of Chloride of Gold being easily reduced by traces of organic matter.

c. *Presence of free Nitrate of Silver on the surface of the Proof.*—It is quite necessary to wash away the free Nitrate of Silver from the pictures before they are immersed in the toning bath, otherwise the Bath will become turbid and discoloured. Nitrate of Silver added to an alkaline solution of Chloride of Gold throws down not only Carbonate of Silver and Chloride of Silver, but also a brown powder, consisting of Peroxide of Gold, or Metallic Gold, and the supernatant liquid contains little else than Nitrate of Soda.

d. *Temperature of the Solution.*—The action of the Bath is much increased by carefully heating it to about 120° Fahr. before the prints are immersed, and this method has also the advantage of bringing the solution at once to the colourless condition, in which it contains more Oxide of Gold and less Chloride of Gold. The plan of warming the Bath, however, is not often adopted by operators, since a similar result can generally be obtained by continuing the action of the cold solution for a longer time.

e. *Additions to the Toning Bath.*—In the Fifth Edition of this Work the Author recommended a toning bath containing a portion of Citrate of Soda in addition to Carbonate of Soda and Chloride of Gold, to be employed in the tepid state. The Citrate was proved by experiment to impart a somewhat brighter tone of purple, and to tend to prevent mealiness and inky tones, but the formula did not come into very general use, since it was found that the same effect could be obtained by preparing the albuminized paper purposely (see page 189).

f. *Presence of Iodide of Silver.*—When Iodide of Silver is present in a proof, the toning action of the alkaline Chloride appears to be less rapid than when the image is formed on Chloride only. Hence sensitive paper is not improved, but rather the contrary, by associating Iodide with the Chloride in salting, as some authors have advised. It is also unwise to employ a Nitrate Bath which has been previously used for Negatives, and contains Iodide of Silver dissolved. On floating the paper upon such a Bath, the Albumen abstracts the Iodide from it in virtue of a chemical affinity, and the printed proof upon such paper remains for a comparatively long time in the toning solution without being coloured by the Gold.

g. *Mode of Preparing the Paper.*—The preparation of the paper is a matter of greater nicety in the alkaline Gold toning process than in the old mode of toning prints by Sulphur, since the affinity which secures the colouring action is stronger in the latter case than in the former. By adding an alkali to Chloride of Gold you improve the colour of the print, but retard the process of colouring, since as before shown the Oxide of Gold produced by the alkali is of itself nearly or quite inert, and the Chlorine is the element which possesses the affinity for Silver, and thus determines the change. Hence although a defective sample of paper may tone evenly in a Sulphur Bath, in the case of the alkaline Gold Bath there would be either spots or markings, which would remain of a red colour and refuse to tone.

One cause of unevenness of toning is an improper mode of applying the Albumen to the paper; for Albumen being a glairy substance, and having a strong tendency to run into lines, much will necessarily depend upon the manipulation. We might indeed remedy this defect by avoiding the use of Albumen, but it is found that in the Chloride of Gold toning process, the proofs acquire an inky shade, unless the image is printed upon the maximum quantity of organic matter, so as to encourage redness as much as possible. A hard-sized gelatinous English paper, with a minimum of Chloride in the salting bath, will produce an agreeable effect, or a foreign starch-sized paper, salted with a mixed Citrate and Chloride. Mr. Waterhouse, of Halifax, gives a formula in which the organic matter is Caseine dissolved in highly dilute potash; there is no gloss, and the finished pictures are of a purple tone. If Albumen be used, the quality of the paper itself will be the principal point to attend to; but, in addition to this, the state of the Albumen must be noted, since sourness and decomposition are injurious not only to the sensitiveness of the paper, but also to the rapidity of toning.

Additional experiments on the conditions of the paper affecting the toning action are much needed. To further their prosecution the Writer ventures to give his experience, as follows:—the more metallic the image, the greater the rapidity of toning by Chloride of Gold, but the more inky the colour. Organic bodies which encourage the production of a subsalt of Silver under the influence of the light, hinder the deposition of Gold, but improve the colour by imparting a shade of red. There are however differences between these organic bodies, ascertainable only by experiment, for although Albumen and Citrate both favour the reduction of the Silver to the state of a subsalt, it will be found on trial that Citrate papers tone with greater facility than albuminized papers. Mr. Mabley, the Honorary Secretary of the Manchester Photographic Society, states that the image tones more rapidly when the paper was excited on a Silver Bath containing a little free Nitric Acid: this accords with theory, because in presence of a strong acid, the reduction approaches more nearly to the state of metal (p. 17), nevertheless the colour so obtained is not agreeable, and a warmer shade will usually be produced by albuminized paper which on its removal from the printing frame exhibits an image of a brick-red, and not of a violet-blue tone.

h. *Time of keeping the Paper.*—If a print be formed upon albuminized paper, and kept for a long time before toning, there will commonly be some difficulty in securing a strong deposit of Gold. This is probably due to a change which takes place in the paper, from the organic matter reacting by degrees upon the Nitrate of Silver, and it has been stated that the same change is more gradually produced when the sensitive papers are preserved for many months in a dry state by means of Chloride of Calcium or Sulphuric Acid; such papers darken in the sun, but if the print be subjected to the action of a Gold toning bath at the same time with one on paper newly sensitized, the latter will be found to tone with the greater rapidity.

SECTION III.

Fixing the Proof.

The conditions for a proper fixing of the proof are not always understood by operators, and consequently they have no certain guide as to how long the prints should remain in the fixing Bath.

The time occupied in fixing will of course vary with the strength of the solution employed: but there are simple rules which may be followed. In the act of dissolving the unaltered Chloride of Silver in the proof, the fixing solution of Hyposulphite of Soda converts it into Hyposulphite of Silver (p. 57), which is soluble in an *excess* of Hyposulphite of Soda. But if there be an insufficient excess,—that is, if the Bath be too weak, or the print removed from it too speedily,—then the Hyposulphite of Silver is not perfectly dissolved, and begins by degrees to *decompose*, producing a brown deposit in the tissue of the paper. This deposit, which has the appearance of yellow spots and patches, is not usually seen upon the surface of the print, but becomes very evident when the print is held up to the light, or if it be split in half, which can readily be done by glueing it between two flat surfaces of deal, and then forcing them asunder.

The reaction of Hyposulphite of Soda with Nitrate of Silver.—In order to understand more fully how *decomposition* of Hyposulphite of Silver may disturb the process of fixing, the peculiar properties of this salt should be studied. With this view Nitrate of Silver and Hyposulphite of Soda may be mixed in equivalent proportions, viz. about twenty-one grains of the former salt to sixteen grains of the latter, first dissolving each in separate vessels in half an ounce of distilled water. These solutions are to be added to each other and well agitated; immediately a dense deposit forms, which is Hyposulphite of Silver.

At this point a curious series of changes commences. The precipitate, at first white and curdy, soon alters in colour: it becomes canary-yellow, then of a rich orange-yellow, afterwards liver-colour, and finally black. The *rationale* of these changes is explained to a certain extent by studying the composition of the Hyposulphite of Silver.

The formula for this substance is as follows:—

$$AgO\ S_2O_2.$$

But $AgO\ S_2O_2$ plainly equals AgS, or Sulphide of Silver, and SO_3, or Sulphuric Acid. The acid reaction assumed by the supernatant liquid is due therefore to Sulphuric Acid, and the black substance formed is Sulphide of Silver. The yellow and orange-yellow compounds are earlier stages of the decomposition, but their exact nature is uncertain.

The instability of Hyposulphite of Silver is principally seen when it is in an isolated state: the presence of an excess of Hyposulphite of Soda renders it more permanent, by forming a double salt, as already described at p. 57.

These facts explain the reason why, in fixing Photographic prints, a brown deposit of Sulphide of Silver sometimes forms in the Bath and upon the picture. To obviate it, observe the following directions:—It is especially in the reaction between *Nitrate of Silver* and Hyposulphite of Soda that the blackening is seen, the Chloride and other insoluble Salts of Silver being dissolved, even to saturation, without any decomposition of the Hyposulphite formed. Hence if the print be carefully washed in water to remove the soluble Nitrate, a comparatively weak fixing bath may be employed. But if the proofs are taken at once from the printing frame and immersed in a dilute Bath of Hyposulphite (one part of the salt to six or eight of water) without any previous washing, *a shade of brown* will be observed to pass over the surface of the print, and a large deposit of Sulphide of Silver will form as the result of the decomposition. On the other hand, with a strong Hyposulphite Bath there will be little or no discoloration, and the black deposit will be absent even when the prints are immersed with the free Nitrate of Silver still upon the surface.

The print must also be left for a sufficient time in the fixing bath, or some appearance of brown patches, visible only on looking through the paper, may occur. Each atom of Nitrate of Silver requires *three* atoms of Hyposulphite of Soda to form the sweet and soluble double salt, and hence, if the action be not continued sufficiently long, another compound will be formed almost insoluble (p. 57) and with a greater tendency to decompose into Sulphide of Silver. Even immersion in a new Bath of Hyposulphite of Soda will not fix the print when once decomposition of Hyposulphite of Silver has commenced. The yellow or brown compound is not entirely soluble in Hyposulphite of Soda, and consequently remains in the paper.

Another important matter to observe in fixing Photographic prints is the *temperature* of the fixing bath. When Hyposulphite of Soda is first dissolved in water, much heat is rendered latent, and the solution in consequence is almost at the freezing point. In this state of things prints are fixed slowly and with difficulty, whereas at 70° or 80° Fahr. the action is more rapid. In the cold winter months Positives should be left in the Bath at least twice as long as in the summer months, to prevent the occurrence of brown patches of imperfect fixation in the substance of the Paper.

The nature of the sensitive surface to be cleared of its superfluous Silver salt must also be considered in estimating the strength of Bath and the time of immersion likely to be required. Albuminized paper, from the horny nature of its surface coating, requires a longer treatment with the Hyposulphite of Soda than plain paper requires; and not only so, but it must be borne in mind that the Albumen has a property of combining with Nitrate of Silver and forming an insoluble salt which is more difficult of solution than Chloride of Silver. Gelatine also combines with Nitrate of Silver, and therefore the mere washing of a gelatinized sensitive paper for a few minutes in cold water does not remove the whole of the free Nitrate. It is better in all such cases to make the fixing bath far stronger than theory would indicate as sufficient for the solution of simple Chloride of Silver, otherwise it will be found that the fixing will be insufficient, and that there will be mealy spots in the print; although on adding recently precipitated Chloride of Silver to the Bath of Hyposulphite it immediately dissolves.

The Writer has noticed that when sensitive paper is *kept for some time* before being used for printing, yellow patches of imperfect fixation are very liable to occur. The Nitrate of Silver appears gradually to undergo a partial reduction by the organic matter, and cannot then be so easily extracted by the fixing bath. It has also been observed that albuminized and salted paper, when kept in a damp place, or exported to warm and damp climates, is liable to undergo a decomposition, in consequence of which the fixing bath fails to extract the whole of the superfluous Silver after printing, and the whites remain discoloured and spotty.

It has been recommended by some writers on Photographic chemistry to saturate the fixing bath with common Salt, in order to convert any Nitrate of Silver left in the proof by imperfect washing, into Chloride, and thus to prevent blackening from decomposition of Hyposulphite of Silver. An excess of salt undoubtedly has the effect thus ascribed to it, but it appears to the Writer that its use is contra-indicated by the fact that Hyposulphite of Soda in presence of Chloride of Sodium is less active as a fixing agent (p. 59), since the Chloride of Sodium exercises an opposing affinity and tends to keep the Silver in the state of Chloride.

For a reason similar to that above assigned, the fixing bath employed for Negatives is a useless addition to the fixing solution for printing, since the Iodide of Sodium present in the former tends to produce yellow patches on the surface of the print; which patches consist of Iodide of Silver in union with Albuminate of Silver or other analogous substances, and these compounds are very difficult of removal by the action of the fixing bath.

ON CERTAIN INJURIOUS CONDITIONS OF THE FIXING BATH.

The object of using the Hyposulphite Bath is to fix the proof by dissolving the unaltered Silver salts, without in any way affecting the image. But it is a fact familiar to the Photographic chemist, that the Hyposulphite of Soda is a substance which very readily yields *Sulphur* to any bodies which possess an affinity for that element; and as the reduced Silver compound in the print has such an affinity, there is a tendency to absorption of Sulphur when the proofs are immersed in the Bath. Hence in many cases a sulphur-toning process is set up, and as the picture is improved by it in appearance, assuming a more purple shade, it is often encouraged by Photographers. Experience however has shown that colours brightened in this way are rendered less permanent, and therefore the careful operator will avoid sulphuration as far as possible. Some of the conditions which facilitate a sulphuretting action upon the proof, and are therefore injurious, are as follows:—

a. *The addition of an Acid to the Bath.*—It was at one time common to add a few drops of Acetic Acid to the fixing Bath of Hyposulphite of Soda, immediately before immersing the proofs. The Bath then assumes an opalescent appearance in the course of a few minutes, and, when this milkiness is perceptible, the print is rendered darker in colour. The chemical changes produced in a Hyposulphite Bath by addition of acid, may be explained thus:—The acid first displaces the feeble Hyposulphurous Acid from its combination with Soda.

Acetic Acid + Hyposulphite Soda.
= Acetate Soda + Hyposulphurous Acid.

Then the Hyposulphurous Acid, *not being a stable substance when isolated*, begins spontaneously to decompose, and splits up into Sulphurous Acid—remaining dissolved in the liquid, and communicating the characteristic odour of burning Sulphur—and *Sulphur*, which separates in a finely divided state and forms a milky deposit. In chemical symbols, $S_2O_2 = SO_2$ and S.

Observe therefore that free acids of all kinds must be excluded from the fixing Bath, or, if inadvertently added, the liquid must afterwards be neutralized by Carbonate of Soda or Chalk.

b. *Decomposition of the Bath by constant use.*—It has long been known that Hyposulphite of Soda undergoes a peculiar change in properties when much used in fixing. The solution when first prepared leaves the image of a red tone, which is the characteristic colour of the reduced Silver Salt, but it soon acquires the property of darkening this red colour by a subsequent communication of Sulphur. Hence a simple fixing bath becomes at last a toning bath, without any addition of Gold. This change of properties has been shown by the Author to be due to a decomposition of Hyposulphite of Silver, and to the consequent formation of a sulphuretting body analogous in its properties to the Tetrathionates.* During the progress of the change Sulphide of Silver is thrown down, forming a black deposit, and the supernatant liquid becomes acid and effervesces on the addition of Chalk. The exact composition of the acid body above mentioned as a product of the spontaneous decomposition of old fixing baths of Hyposulphite is not known, but the effects it produces on the prints are well understood, and can be shown to be most injurious; for it not only blackens the shadows of the picture by communicating Sulphur, but causes a solution of the middle tints, and destroys the pure white colour of the high lights.

In order to avoid the formation of this acid substance in the Bath, it is most important to wash away all the free Nitrate of Silver; and hence one advantage of the alkaline Gold toning process over the old methods, since this process cannot be carried on unless the free Nitrate of Silver be first washed away. Another precaution is to keep the Bath shielded from a very strong light, and to put it away in a cool place: light and heat both favour the decomposition of Hyposulphite of Silver and cause a black deposit to be thrown down.

A more practical means of preserving a fixing bath for a long time in a state in which it communicates but little Sulphur to the proof is the addition of an *alkali*. The Author showed in his early papers on the Tetrathionates and their reaction with Hyposulphite of Soda that alkalies decompose the unstable sulphuretting principle. Hence if the Bath be treated with Potash or Carbonate of Soda, an alkaline *Sulphide* is gradually formed, which precipitates Sulphide of Silver, and in the course of a few days the liquid returns to its original condition and ceases to act as a toning agent upon the proof. Here we see another point of excellence in the alkaline Gold toning process, since each print carries with it small doses of Carbonate of Soda, which effectually prevent the formation of acid in the Bath.

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* See 'Journal of the Photographic Society,' September and October 1854.

SECTION IV.

On the Fading of Photographic Prints.

For many years subsequent to the discovery of the process of Photographic Printing by Mr. Fox Talbot, it was not generally known that pictures so produced were easily susceptible of injury from various causes, and in particular from traces of the *fixing-agent* remaining in the paper. Hence, due care not being taken in the proper cleansing and preservation of the proofs, the majority of them faded.

The present Section is intended to explain practically and in a concise manner the causes of the fading of Photographic Prints, and the precautions which should be taken to ensure their permanency.

a. *Imperfect washing.*—This is perhaps the most important cause of fading and the most frequent. When Hyposulphite of Soda is allowed to remain in the paper, even in minute quantity, it gradually decomposes, with liberation of Sulphur, and destroys the print in the same way and quite as effectually as a solution of Sulphuretted Hydrogen or an alkaline Sulphide.*

Imperfect washing may be suspected, if the Photograph within a few months from the date of its preparation, *begins to get darker in colour:* the half-tints, which are the first to show the action, afterwards passing into the yellow stage, whilst the dark shadows remain black or brown for a longer time.

The proper mode of washing Photographs is sometimes misunderstood. The length of time during which the print lies in the water is a point of less importance than the continual changing of the water. When a number of Positives are placed together in a pan, and a tap turned upon them, the circulation of fluid does not necessarily extend to the bottom. This is proved by the addition of a little colouring matter, which shows that the stream flows actively above, but at the lower part of the vessel, and between the prints, there is a stationary layer of water which is of little use in washing out the Hyposulphite. Care should therefore be taken that the pictures be kept as far as possible separate from each other, and when running water cannot be had, that they be frequently moved and turned over, fresh water being constantly added. When this is done, and especially if the *size* be removed from the paper in the manner presently to be advised, four or five hours' washing will be sufficient. It is a mistake to allow the pictures to remain in the water for several days; which produces no good effect, and may tend to encourage a putrefactive fermentation, or the formation of a white deposit upon the image when the water contains Carbonate of Lime.

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* The reason why the long-continued action of Sulphur fades the print, has already been indicated at p. 191. It is because the amount of real Silver in the image is very small, and Sulphide of Silver in minute quantity appears pale and yellow.

Mr. Maxwell Lyte states that traces of soluble Chloride left in the paper are injurious to the permanency of Photographic prints: this indicates the propriety of avoiding the use of water too highly charged with saline matter, and of finishing the washing with a bath of rain water.

b. *Atmospheric Oxidation.*—Upon examining collections of old Photographs, it is not uncommon to find prints which are stated to have remained unaltered for a long while after their first production, but in the course of time to have lost their brilliancy, and become pale and indistinct. This kind of fading often commences at the corners and edges of the paper, and works inwards towards the centre; it is principally caused by a slow process of *oxidation*.

Sulphuration in the process of toning, which has before been shown to occur when old and decomposed solutions of Hyposulphite of Soda are employed, always facilitates subsequent oxidation and yellowness. It is indeed difficult to avoid *slight* sulphuration unless fresh solutions of Hyposulphite are employed in fixing, but the remarks now made on the injury caused by Sulphur, refer to its full action.

Moisture greatly hastens the yellow change due to atmospheric oxidation, and hence a state of comparative dryness may be said to be essential to the preservation of all Photographs. In collecting evidence upon the subject, "wet" and "damp" are frequently alleged as having been causes of fading;—the prints were hung against a damp wall during frosty weather, in a room without a fire; or the rain had been allowed to penetrate the frame!

Acid matters, and also other bodies which dissolve Oxide of Silver, such as Ammonia, etc., favour oxidation when left for a long time in contact with the image. The materials often used in sizing papers, such as Alum and Resin, being of an acid nature, are ultimately injurious to the image; and the removal of the size, which may easily be effected by means of hot water, without much injury to the tint, has the additional advantage of carrying out the last traces of Hyposulphite of Soda, and also the germs of *fungi*, which, if allowed to remain, would vegetate and produce a destructive mouldiness.

The fact that acids facilitate oxidation of the image suggests also that Photographic Prints should not be handled too frequently, or touched with the finger more than is necessary; the warm hand may leave behind a trace of acid* which would tend in time to produce a yellow mark. For the same cause they ought not to be laid down carelessly in any place likely to communicate impurity.

The employment of albuminized paper confers a positive advantage in protecting the image from oxidation: this was proved by careful experiments performed with various oxidizers. The use of Albumen indeed gives the main chance of preventing a print which has been toned to blackness by sulphur, from gradually becoming pale and yellow by atmospheric oxidation.

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* The Writer has seen blue litmus-paper immediately reddened by being laid upon the arm of a person suffering from acute Rheumatism. This acid is probably Lactic Acid.

c. *Improper modes of Mounting the Proof.*—This cause of change might have been included with the last, since the fading of badly mounted prints is usually due to atmospheric oxidation. All cements which are of an acid nature, or which are liable to become *sour* by acetous fermentation, should be avoided. Flour paste is especially injurious, and many cases of fading have been traced to this cause. The addition of Bichloride of Mercury, which is often made to prevent the paste from becoming mouldy, still more unfits it for Photographic use. No substance appears better than Gelatine, which does not readily decompose, and shows no tendency to absorb atmospheric moisture. The *deliquescent* nature of many bodies is a point which should be borne in mind in mounting Photographs, and hence the use of a salt like *Carbonate of Potash*, which the Writer has known to be added to paste to prevent the formation of acid, would be unadvisable.

d. *The effect of Imperfect Fixation.*—The earlier Photographers did not always succeed in properly fixing their prints, and old Photographs are often found thickly studded with spots and blotches in the tissue of the paper. These prints, however, are not invariably faded upon the surface, and hence it cannot be said that imperfect fixation will certainly end in the total destruction of the picture. Still a notice of the subject may properly be introduced in this place, and the attention of the reader be once more drawn to the importance of examining each print by holding it against the light: imperfect fixation will be shown by yellow patches in the body of the paper.

e. *Impurities in the Air.*—A Photograph carefully prepared may suffer injury from deleterious matters often present in the atmosphere. The air of large cities, and particularly that emanating from sewers and drains, contains Sulphuretted Hydrogen, and hence articles of silver-plate become tarnished unless placed beneath glass. The injury which a print sustains by exposure to air contaminated with Sulphuretted Hydrogen, is less than the tarnish produced upon the bright surface of a silver plate; but it is recommended as a precautionary measure, that Photographic Pictures should be protected by glass or kept in a portfolio.

The products of the combustion of coal-gas are probably more likely than the cause last named, to be a source of injury to Photographs suspended without any covering. The sulphur compounds in gas burn into Sulphurous and Sulphuric Acid, the latter of which, in combination with Ammonia, produces the sparkling crystals often observed upon the shop windows.

The question as to the manner in which the Photographic image may best be protected from these extraneous causes of fading has been mooted, and many plans of coating prints with some impervious material have been devised. If the pictures are to be glazed or kept in a portfolio, this of itself will be sufficient, but in other cases it may perhaps be useful to apply a layer of spirit or gutta-percha varnish. The use of wax, resin, and such bodies is likely, by introducing impurities, to act injuriously rather than otherwise.

g. *Decomposition of Pyroxyline a source of injury to Collodion Photographs.*—Although the present Section refers more especially to Photographic prints on paper, yet a few remarks upon Collodion images may not be out of place. Collodion Positives and Negatives are usually esteemed permanent; but some have been exhibited which, having been put away in a damp place, gradually became pale and indistinct. The change commences at rough edges and isolated points, leaving the centre, as a rule, the last affected. On examination, numerous cracks are often visible, thus indicating that the Collodion film has undergone decomposition, and has liberated corrosive Oxides of Nitrogen. Substitution compounds containing Peroxide of Nitrogen are known to be liable to spontaneous change. The bitter resin produced by acting upon white sugar with Nitro-Sulphuric Acid, if not kept perfectly dry, will sometimes evolve enough gas to destroy the cork of the bottle in which it is placed; the solution of the resin has then a strong acid reaction, and rapidly fades an ordinary Positive Print.

[illegible] and indicate that Collodion [illegible] themselves the elements of their [illegible] protected from moisture by a coating [illegible]

[illegible] — The Photographic prints [illegible] in the same manner as fugitive [illegible] to light and air. Bottles [illegible] were placed [illegible] house with a southern aspect, for [illegible] whatever could be [illegible] and others kept in [illegible] which is the [illegible] which cannot alto[illegible] to inquire what mode [illegible] stability.

[illegible] light and sub[illegible] may be expected [illegible] sun-prints; not that [illegible] the chemical composition [illegible] necessarily peculiar, but that [illegible] increase the intensity [illegible] and to add to its stability [illegible] This point has not [illegible] recommended to [illegible] solution which is [illegible] and to produce [illegible] for this [illegible] results as regards colour [illegible] the advantage [illegible] the saturation of a Ne[illegible] as regards perma[illegible] print received

[illegible] which the latent [illegible] next to [illegible] the difficulty of ob[illegible] in Silver, will [illegible]

Great stress has been laid upon the superior permanency given by the use of Gold in toning, but the fact appears to be that the Gold is precipitated in so small a proportion upon *the lighter shades* of the proof, that it cannot be expected to preserve them from any destructive agencies. It will be sufficient if the toning and fixing can be fully effected without any real injury from communication of Sulphur.

The prints which are *least stable* are such as have been toned in *acid Hyposulphite Baths, without Gold;* and the difficulty of preserving such pictures from becoming yellow in the half-tones is very great. All those plans of toning in which Acetic or Hydrochloric Acid is mixed with Hyposulphite of Soda, and the Positive immersed whilst the liquid is in a milky state from precipitation of Sulphur, ought studiously to be avoided.

Mode of testing the permanence of Positives.—The tests for Hyposulphite of Soda are not sufficiently delicate to indicate with certainty when the process of washing has been properly performed. The quantity of that salt left in the paper is usually so small and so much mixed up with organic matter, that the application of Protonitrate of Mercury or of Nitrate of Silver to the liquid which drains from the corner of the print, would probably mislead the operator.

A dilute solution of Permanganate of Potash, prepared by dissolving half a grain, or from that to two grains of the salt, according to its purity, in one gallon of distilled water, affords a convenient mode of testing Positives as regards their power of resisting oxidation; and to an experienced eye it will prove the presence or absence of Hyposulphite of Soda, the smallest trace of which is sufficient to remove the pink colour of the Permanganate. The Positives must be moved occasionally, as the first effect is to decolorize a portion of the liquid, the Permanganate oxidizing the size and organic tissue of the paper. After an immersion of twenty minutes to half an hour, varying with the degree of dilution, the half-tones of the picture begin to die out, and the full shadows become darker in colour. The bronzed portions of the print withstand the action longer, but at length the whole is changed to a yellow image much resembling in appearance the Photograph faded by Sulphur.

The most available and simple plan of testing permanence is to enclose the pictures in a stoppered glass bottle with a small quantity of water. If they retain their half-tones after a course of three months of this treatment, and do not become mouldy, the mode of printing followed is satisfactory.

Boiling water will also be found useful in distinguishing the unstable colours produced by Sulphur from those following the judicious employment of Gold; in all cases the image will at first be reddened by the hot water, but if toned without Sulphur it will, as a rule, recover much of its dark colour on drying.

A solution of Chromic Acid may also be applied to distinguish prints toned by Sulphur from others toned by Gold; the presence of metallic Gold protecting the shadows of the picture in some measure from the action of the acid.

The solution should be prepared as follows :—

Bichromate of Potash	6 grains.
Strong Sulphuric Acid	4 minims.
Water	12 ounces.

The characteristic appearance of prints which have been much sulphuretted, and are very liable to fade, should be known. A yellow colour in the lights is a bad sign; and if the half-tones are at all faint and indistinct, with an aspect of commencing yellowness, it is almost certain that the Positive will not last for any considerable length of time.

CHAPTER IX.

COLLODION PRESERVATIVE AND DRY COLLODION PROCESSES.

The object of the "Collodion Preservative" and dry Collodion Processes is to maintain the sensitiveness of the film for a certain length of time after it has been excited in the Bath. There is some difficulty in effecting this, because if the plate be allowed to dry spontaneously, the solution of free Nitrate of Silver upon its surface, becoming concentrated by evaporation, eats away the Iodide of Silver, and produces transparent spots (p. 130).

Some operators have attempted to use a second plate of glass in such a way as to *enclose* the sensitive film, with an intervening stratum of liquid. The difficulty however of separating the glasses again without tearing the film, is considerable.

In the process of Messrs. Spiller and Crookes, the property possessed by certain saline substances of remaining for a long time in a moist condition was turned to account. Such salts are termed "deliquescent," and many of them have so great an attraction for water that they absorb it eagerly from the air; the solution having been formed, the water cannot entirely be driven off except by the application of heat. In selecting a deliquescent salt for a Preservative Process, it is necessary to choose one which produces no precipitate in solution of Nitrate of Silver, such for instance as the Nitrate of Magnesia, or the Nitrate of Zinc. Deliquescent bodies like Chloride of Calcium or

Carbonate of Potash, which decompose Nitrate of Silver, are inadmissible, since it is found that they destroy the sensitiveness of the film, as will presently be shown.

The process of Spiller and Crookes, although it had the great merit of originality, was soon superseded by others, since it appeared that plates preserved by Nitrate of Magnesia were liable to yield feeble and imperfect Negatives, unless the Collodion and Bath happened to be in a peculiar condition. This defect, together with occasionally fogging of the transparent parts, the Author believes to have resulted from the employment of an *inorganic* instead of an organic preservative agent.

The attention of experimenters in the Preservative Processes was also directed to Glycerine, as a substance with little or no action on Nitrate of Silver, and therefore one likely to succeed. Glycerine failed however to give any certain results, and often produced a weak and foggy picture, like the inorganic salts before alluded to.

The first use of *Honey* as a preservative agent was proposed by Mr. Shadbolt. This substance was deemed by some to be unsuitable, since Grape Sugar, always present in it, reduces Nitrate of Silver to the metallic state: the results however showed that plates prepared with Honey, yielded more vigorous, and also cleaner Negatives than those made with Glycerine or Nitrate of Magnesia. The reason of such an apparent anomaly will be understood, when it has been shown, a few pages in advance, that a preservative substance possessing reducing power on Salts of Silver is precisely what is required, and that a neutral body like Glycerine, which does not reduce Nitrate of Silver, is incapable of acting as a stimulus to the actinic change.

Honey employed as a preservative substance varies much in its action with the extent to which the plates are washed from the Nitrate of Silver before the Honey is laid on. In proportion as the quantity of free Nitrate is large, both sensitiveness and intensity are increased, but the keeping qualities of the plates are diminished. This is especially the case in hot weather, and it will then frequently happen that in the course even of a few hours, an incipient decomposition will be set up, so that after the exposure of the film in the Camera, the developing solution brings out an intensely red and solarized picture, with a universal deposit of Silver upon its surface, sufficient to render the picture invisible by reflected light. Honey in fact being a slow reducing agent, although it exerts in the first instance a positive action in keeping the shadows of the image clean, yet afterwards sets up decomposition, and gives rise to fogging.

In order to employ the preservative Honey in an advantageous manner as regards keeping properties of the plate, the Collodion film should be freed more or less completely from the soluble Nitrate of Silver: the Grape Sugar has then only the pure Iodide and Bromide of Silver to act upon, and no decomposition takes place. This is the plan followed in the "Oxymel" process of Mr. Llewelyn, in which also the Honey is acidified by Acetic Acid, in order still further to lessen the chances of failure from incipient reduction of Nitrate of Silver.

The Oxymel process, although free from the peculiar defects of the original Honey process, is however open to others of an opposite kind, for it is found that the presence of small quantities of free Nitrate of Silver is useful in the Honey process in increasing sensitiveness and intensity of image; hence when the plates are fully washed, the film not only takes the Camera impression very slowly, but the image developes of a blue or slaty tone instead of a brown or red tone. Thus it is perceived that long keeping properties are, in this process, irreconcilable with other good qualities, and therefore we naturally turn to the consideration of a purely dry process: in this case all moisture being removed, and the chemical decompositions being in consequence nearly suspended, we are enabled to avail ourselves of those conditions which secure a rapid and intense action, without at the same time endangering the stability of the excited film.

Dry Collodion processes.—Formulæ for operating with a dried film of Collodion have been given at various times in the foreign journals; in some of which it is stated that nothing is required but mere washing with water after taking the film from the Bath. Success by this mode, however, is quite problematical, and can only be expected when either the Collodion or Bath is in a particular state of organic change. It has now been clearly determined that a film of Iodide of Silver upon Collodion will not uniformly yield a perfect Negative after removal of the Nitrate of Silver and desiccation. On applying the reducing agent to such a plate, previously exposed in the Camera, we see at once that the particles of Iodide have not been thrown into the exact condition requisite to obtain a rapid precipitation of Silver in the black form, and consequently the action is irregular and fogging ensues: Organic matter in some shape appears to be necessary in a dry process manipulated in the ordinary way.

The most simple dry Collodion process in which the necessity for organic matter is recognized, is that of the Abbé Despratz, who dissolves common rosin in iodized Collodion, and washes the excited film with water after removing it from the Bath. An exposure in the Camera ot not more than twice the length required for wet Collodion is then given, and the plate is re-dipped for an instant in the Nitrate Bath: after this the image comes out on flooding the plate with Pyrogallic Acid in the usual way. Although the Writer is not able to state that this process will yield *clear* Negatives with certainty, yet he is convinced that a remarkable effect is produced by this second dip in the Nitrate Bath. Theory might at first suggest that the restoration of the Nitrate of Silver, previously removed by washing, was the only object attained, but it is not so, for the image cannot be developed after so short an exposure when Pyrogallic Acid and Nitrate of Silver are mixed and applied simultaneously to the plate. It seems probable therefore that the exposure in the Camera sets up a molecular disturbance, not in itself sufficiently decided to produce quick development, but capable of being increased, or carried into a further stage by contact with Nitrate of Silver. It has however been shown, on the other hand, that the application of Nitrate of Silver will nearly destroy the highest lights of an invisible image on a plate left in the Camera for a longer time than in the last experiment, and hence we can only conjecture that there exists an alternating action of the light, and that the same chemical agent may produce opposite effects according to the stage at which it is applied to the plate (p. 39). This subject is still involved in much obscurity, and deserves further investigation.

To all dry processes like that of the Abbé Despratz, in which the organic matter is added to the Collodion, there exists one serious objection, viz. that the Nitrate Bath gradually suffers deterioration in consequence of the organic substance dissolving out of the film (p. 136). The Photographic properties of the solution are not immediately injured thereby, if a bromo-iodized Collodion be employed (p. 158), but with a simply iodized Collodion used in the ordinary wet process, either a general fogging of the film, or some other disturbance of the development, will soon be perceived. It appears therefore more desirable, as far as the integrity of the Nitrate of Silver is concerned, to apply the requisite organic body to the excited film subsequent to its removal from the Bath.

Taupenot's Collodio-Albumen process follows next in order of discovery. It is not altogether a Collodion process, nor is it entirely a process on Albumen, but rather a union of the two. The manipulations are double throughout—a sensitive film of Iodide of Silver in Albumen being placed upon a film of Iodide of Silver in Collodion. The two together offer advantages which cannot be obtained by the use of either separately, for the presence of the Albumen secures a vigorous development, whilst the substratum of Collodio-Iodide adds to the sensitiveness. There are two Nitrate Baths in this process, one for the Collodion, and the other for sensitizing the dry film of iodized Albumen. There are also two operations of washing; the first, as before, for the Collodion, and the other for removing the excess of free Nitrate from the Albumen.

The Collodio-Albumen process of M. Taupenot is undoubtedly a troublesome one, but it is perhaps more to be depended on than any other known, inasmuch as it is independent of the exact physical and chemical condition of the Collodion. In dry processes generally, the state of the Collodion must be carefully attended to, as will presently be shown, but the Taupenot method is rather an Albumen than a Collodion process, since the substratum of Iodide upon Collodion is used merely for the purpose of increasing the sensitiveness. A facility in receiving the latent impression is indeed a matter of importance in any dry process, but less so than a correct development, because in the one case a few minutes longer in the Camera prove a remedy, whereas in the other no simple remedy is known. Albumen therefore still maintains its ground, because the Photographer finds by experience that he can rely upon it for controlling the action of his reducing agent, and producing the chemically opaque image.

Our knowledge of the theory of dry Collodion has been much assisted by the researches of Dr. Hill Norris. His view of the function of a preservative substance applied to the excited film was that it acted by keeping open the pores of the Collodion: Pyroxyline forms a gelatinous layer, which is soft and spongy when wet but shrinks on drying, and after it has been once dried, it does not return to its former pappy condition on being a second time wetted with water. In order therefore to secure that penetration by the developer which is requisite for the rapid bringing out of the picture, some such substance as Gelatine or Albumen is required, capable of insinuating itself between the particles of the Iodide, and so of preventing them from collapsing and producing a surface impervious to liquids. Norris did not consider the presence of free Nitrate of Silver to be necessary in a dry process, but rather detrimental, and advised that the plates should be perfectly washed with distilled water previous tò the application of the Gelatine. Another point on which great stress was laid was the *physical condition of the Collodion:* it ought not be of the kind which gives a horny film, but rather of the *powdery* variety, the properties of which are described at p. 109; less difficulty would then be experienced in maintaining the conditions previously insisted on.

The above views on the theory of dry processes have never been disputed, but it was soon found that they embraced only a portion of the truth; for the same certainty was not obtained by the method of Norris as by that of Taupenot, and with some samples of Collodion, apparently in the proper physical state, only faint Negatives could be produced.

The next decided step in the theory of dry Collodion was the discovery of the method known as the "Fothergill process," in which diluted Albumen was poured over the plate, and afterwards washed off again with water. This process proved to be less dependent upon the particular state of the Collodion than that of Dr. Norris, since intense Negatives were obtainable both with horny and porous Collodion films. It was found advisable however as a rule to avoid washing the film too closely with water before the Albumen was applied; or, in other words, to leave a little free Nitrate of Silver with which the organic substance might combine. The theory therefore was stated as follows:—In the wet Collodion process the presence of free Nitrate of Silver imparts an increased sensitiveness to the film of Iodide of Silver: in the Fothergill process a portion of this free Nitrate is converted into Albuminate of Silver, and the remainder is removed by washing with water.

Observe certain points of difference between the dry process of Norris and that of Fothergill. In the former you remove the whole, and in the latter only a part, of the free Nitrate of Silver. In the Norris process also the Gelatine preservative is left upon the film, whereas in the Fothergill process the greater part of the Albumen preservative is washed away. Hence a Norris plate has the pores of its collodionized surface filled up with the organic substance, so that although the film contracts on drying, it softens and swells up again when it is wetted previous to development; but in the Fothergill plate the quantity of Albumen which remains upon the Collodion after the second washing is so small, that the film once dried does not again expand fully on being wetted, and the action of the developer is in consequence confined nearly to the surface. For this reason a Fothergill plate must be under a disadvantage as regards rapidity of development, since the solution of Pyrogallic Acid cannot penetrate deeply, and the image has to be built up by superposition of metallic particles. Porosity being wanting in this process, we have to trust to the extraordinary capabilities of Albumen before alluded to, to supply the deficiency; and since the controlling action of Albumen upon the development is more decidedly seen when it is previously combined with Nitrate of Silver, a little free Nitrate should always be left upon the plates before albuminizing.

The views above expressed will not perhaps tally with the experience of all who practise the Fothergill process, since it is recommended by some to remove *the whole* of the Nitrate of Silver from the plate before applying the Albumen. This plan is indeed favourable as regards long-keeping properties, because Albumen when combined with Nitrate of Silver, tends to reduce it by degrees to a Sub-Albuminate even in the dark. It is however *un*favourable as regards the sensitiveness, and also as regards the intensity of the developed image. If any should assert the contrary, we invite them to examine more closely the conditions under which their experiments were performed: probably they will find that they have employed a Collodion in a state of organic decomposition; and such a Collodion, as we shall presently show, is capable of supplying in a measure the place of the Albumen, and, even when dried, of yielding a Negative without any preservative.

If the Fothergill process is to be assimilated to that of

Taupenot, and to be considered as an Albumen process, nearly independent of the state of the Collodion, it cannot be too strongly insisted on that the Albumen left upon the film must be coagulated with Nitrate of Silver. Herein however lies the practical objection to this process, for it is not by any means an easy matter to apply Albumen *evenly* to the surface of a large plate, unless the whole of the Nitrate of Silver be previously removed by washing. Albumen precipitates Nitrate of Silver, and hence in the ordinary mode of manipulating Fothergill plates, it is a common circumstance to encounter stains and markings of shapes varying with the structure of the Collodion and the manner of pouring on the Albumen.

Messrs. Petschler and Mann, members of the Manchester Photographic Society, have lately described a modified dry method which appears to occupy an intermediate position between the process of Taupenot and that of Fothergill. The excited Collodion film, after a careful washing in water, is coated with diluted Albumen containing Chloride of Sodium or Ammonium, and is then dried with the Albumen still remaining upon its surface. In this state light has but little action upon it, since it appears that dry Iodide of Silver, in contact with Chloride of Sodium, is comparatively insensitive. To render the plates again sensitive to light, they are abundantly washed with water, and then dried a second time.

The above process differs from that of Taupenot in the omission of the second Bath of Nitrate of Silver; the objection to the use of which is, that it soon decomposes under the reducing influence of Albumen dissolved out of the plates, and a surface-scum in consequence forms, thus originating stains. Another effect due to decomposition of Nitrate of Silver by Albumen, is a tendency to rapid discoloration in the mixed developer, and a difficulty in keeping the shadows clean, and free from deposited Silver. In discarding the second Bath we gain therefore important advantages, but the fact cannot be concealed that as regards a constant intensity of the image we are more dependent upon the state of the Collodion than before, since Albumen appears to increase the vigour of the impression in the Camera more decidedly when it has been coagulated by Nitrate of Silver.

The new method resembles that of Fothergill in the plates being washed with water after the application of the Albumen, but differs from it in the fact that the Albumen is allowed to become dry before the water is again applied. This difference is important, because the effect of drying is to render the Albumen less soluble, so that the second application of water removes only a portion of the organic substance. The fact of the plates regaining a considerable sensitiveness after the second washing cannot easily be explained, except on the supposition that the porosity of the film is preserved in a measure by a part of the Albumen remaining upon the Iodide, for we know that in the Fothergill process, if the Albumen be washed away whilst wet, and no free Nitrate of Silver be present to coagulate and retain a portion of it, the sensitiveness will be lessened.

A dry process has been lately described by Major Russell, in which we recognize a new principle. The preservative material is *Tannin*, and the plates are entirely freed from Nitrate of Silver, in the same manner as in the process of Norris. Tannin is very soluble in water, and its aqueous solution on evaporation leaves a film of varnish which is not sticky to the touch. When applied to the surface of the excited film the Tannin keeps open the pores of the Collodion as before described, and the mechanical condition of the film appears to be intermediate between that of Norris and Fothergill, being slightly more permeable than the latter, but considerably less so than the former.* Independently of this, however, Tannin has a very remarkable effect in *stimulating* the sensitive Iodide, and causing it to take a much deeper and more decided impression in the Camera. It would not be correct to speak of this acceleration as an increased sensitiveness imparted to the Iodide, but rather as an augmentation in the force of development, in consequence of which the image starts out quickly, and with more contrast between the extreme tints: the colour of the image is also different, the particles which compose it being no longer grey and crystalline, but finely divided and opaque, so that the Negative possesses all those qualities which the Photographer requires.

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* When the porosity of a film of dried Collodion is fully maintained by the application of a glutinous preservative, it changes colour on being wetted with water, losing the pale opaline appearance which it had acquired by drying, and returning again to the yellow creamy aspect of a recently prepared plate. A film of Collodion not kept open by a preservative becomes pale and blue on drying, and remains so even after wetting.

It would involve the reader in endless perplexity were we to attempt to trace the exact origin of the process now under discussion, for it cannot be denied that Tannin and Gallic Acid are photographically similar, and that Gallic Acid upon the film was employed by Talbot, and also by Archer and others who followed him. In the "Talbotype," however, the Gallic Acid was conjoined with Nitrate of Silver, and also with Acetic Acid, the latter being used to maintain the balance and prevent a too speedy reduction. Russell in applying the method to Collodion modifies it in such a way as to suit the altered requirements of the process, eliminating the Nitrate of Silver and dispensing with the Acetic Acid: then in order to overcome the tendency which Gallic Acid exhibits to crystallize on drying, he substitutes Tannic Acid, and thus secures the mechanical conditions of permeability by aqueous liquids.

Let us explain at greater length the mode in which we suppose this new Photographic chemical to act. Tannin is a reducing agent: if you mix it with solution of Nitrate of Silver in a test-tube, in the course of an hour or two the sides of the tube will be silvered like a mirror. Now it is known that moist Iodide of Silver on Collodion is active in presence of free Nitrate of Silver, but that dried Iodide of Silver on Collodion is actinically sluggish: although capable of receiving an impression in the Camera, the latent image is so faint that it cannot be developed in a satisfactory manner. The addition of free Nitrate of Silver in anything like quantity is not admissible in a dry process, since it dissolves the sensitive Iodide and converts it into an Iodo-Nitrate of Silver. *An organic reducing agent* appears to be capable of supplying the place of free Nitrate of Silver, and of causing the Iodide to assume that peculiar condition in the Camera, which leads to a precipitation of Silver in the black form on the application of the mixed developer.

It had been supposed by many that the employment of substances like Gallic Acid or Tannin in a dry process would lead to a general clouding of the film: so far, however, from such being the case, it is a fact that they preserve the transparency of the shadowy portion of the Negative. The phenomenon known as *fogging* may, as we have shown at page 47, be originated by opposite causes. One form of this defect is due to an excess of action of the chemicals, and is remedied by the use of a retarding acid; but another kind of fogging is caused by defective action, and a remedy for this is the use of *a reducing agent* applied to the film before exposure. Every skilful Photographer knows that in the wet process too much Nitric Acid in the Negative Bath is a cause of fogging almost as decided as an excess of the alkali Ammonia; and so in the dry process, if the Iodide be used in too languid a state, so to speak, it will be impossible to obtain a clean picture, because the latent image being imperfectly formed, the developer finds no definite surface upon which to exhaust its energies (see p. 48). Those who pay but little regard to theoretical considerations in Photography, and are guided solely by practice, will be convinced on trying the following experiment:—Take a dry Collodion plate prepared with a simple preservative solution of four grains of Gelatine to the ounce of Water: then apply to one half of this plate a saturated solution of Gallic Acid; dry and expose as usual. A single trial will be sufficient to indicate a surprising difference between the two halves, not only in depth and rapidity of development, but also in the brilliancy and sharpness of the whole picture. In the one case there will probably be indistinctness in the lines, and fringes or halation round the shadows, whilst in the other the deposit of Silver forming the image will be regular and uniform, being limited exactly to those parts which have been touched by light. This effect could not be obtained by the use of a body like *Glycerine*, which is miscible with Nitrate of Silver without change, but according to the experience of the Writer is confined to the organic substances which give intensity in the dry processes, and are characterized by decomposing Nitrate of Silver, or by entering into some form of combination with it.

Another inconvenience originally anticipated from the use of reducing agents in dry Collodion Photography was a deficiency of keeping properties. This however has, like the last, proved to be an unfounded apprehension. It would not be safe to leave Gallic Acid and Nitrate of Silver together upon the excited film, but when the last portions of free Nitrate of Silver have been removed by a Bath of Salt and Water, the plates will retain their properties unchanged for a length of time amply sufficient for all practical purposes.

Collodion for the Dry Processes.—The above sketch of the theory of dry Collodion would be incomplete without a few remarks upon the composition of the Collodion itself. What is the reason of the difficulty which has always been experienced in employing films of dry Collodion? Iodide of Silver upon desiccated Albumen was used successfully from the first: why then should it not be so when supported by Pyroxyline? Doubtless the close and parchment-like texture of dry Collodion and its impermeability by aqueous liquids constitutes a difficulty, but another and more serious impediment lies in the fact that Collodion is too similar to Glycerine and bodies of that class, before mentioned as being neutral and indifferent to the Salts of Silver. When iodized Albumen is dipped in a Nitrate Bath, the substance precipitated in the film is not pure Iodide of Silver, but Iodide of Silver associated with Albuminate of Silver, probably in the form of a double compound. This body is highly photographic, and takes a strong invisible impression in the Camera, even after the free Nitrate of Silver has been washed away. Iodized Collodion, on the other hand, throws down a purer form of Iodide in its passage through the Bath, and this Iodide when washed and dried, does not take a strong impression in the Camera. Comparing the Collodion film with the Albumen film, we find that the luminous image affects the former with greater rapidity, but not with equal force. The depth of the latent impression on pure dry Collodion, never increases uniformly with the intensity of the light, and hence there is an imperfect gradation of tone; also the image is easily reversed by over-exposure, so that on developing, a transmitted Positive is obtained instead of a Negative. It may be taken to be an established fact that a body possessing organic reactions towards Salts of Silver ought to be in contact with the Iodide during its formation in the Bath, if that Iodide is to be precipitated in a state photographically available after drying. Fortunately it is in our power to modify Pyroxyline, and to impart to it a certain measure of those organic reactions which it lacks when existing in a pure form. Let us explain briefly how this may be effected. Cellulose possesses an appreciable affinity for Nitrate of Silver, although less than that of Albumen or Gelatine: this affinity it loses when converted into Pyroxyline. If however the proportions of the constituents of the Nitrosulphuric Acid be purposely varied, and the temperature of the acid at the same time raised, a partial conversion of the Cellulose into vegetable parchment, or into Grape Sugar takes place, and it is then found that the resulting Pyroxyline is no longer indifferent to the Salts of Silver, but has acquired the property of retaining a small portion of Nitrate of Silver after passing through the Bath. Thus the modified Pyroxyline becomes assimilated to Albumen in its Photographic reactions, and when iodized throws down no longer a pure and isolated Iodide of Silver in the Bath, but an Iodide of Silver associated with traces of an organic compound of Silver. If the reader should fail in comprehending how the presence of mere traces of an organic Salt of Silver in a Collodion film can have any effect upon the image, let him make the simple experiment of dissolving *Glycyrrhizine*, or Sugar of Liquorice, in iodized Collodion, and of testing the Photographic effect before and after: he will find that a fractional part of a grain of the Sugar will make all the difference between a feeble and an intense Negative.

Another means of altering Collodion in such a manner as to render it available in the dry processes, is by keeping the Collodion for a time in the iodized state. We have already shown, in the Chapter on Negatives, that Collodion, however iodized, may be expected to produce a more vigorous picture after keeping; but in the dry process this effect is even more decidedly seen than in the wet process. In both cases there is a slow and gradual decomposition of the Pyroxyline under the influence of the base of the Iodide, the effect of which is to give the former an increased power of uniting with Nitrate of Silver. In the dry process however the efficiency of the film is still further augmented by the fact that iodized Collodion loses by age a portion of its horny quality, setting less firmly upon the glass, and presenting a more open and spongy surface, so as to admit of the glutinous organic substance penetrating between the separate particles of Iodide, and thus preserving a passage for the developer.

Our general conclusions on the subject of Collodion for the dry processes may be recapitulated as follows:—The "organic" element is always needed in the sensitive film. If it exist already in the Collodion itself through decomposition after iodizing or other causes, it will scarcely be required in an extraneous form; and in such a case it will only be necessary to wash and dry the film, supposing it to be a porous Collodion, or to flood it with a simple glutinous solution if it be a horny Collodion. When however the Collodion is more pure, and hence deficient in those qualities which give intensity to the development, the lacking element must be supplied in the form of a preservative, and of all the substances commonly employed for that purpose, Albumen and Tannin are the most decided in their action, the former being supposed to be coagulated by Nitrate of Silver; other preservatives, such as Dextrine, Cane Sugar, and Gum, are only effective when the Collodion is able of itself to supply a part of the lacking element, and merely requires assistance to enable it to complete the remainder.

The Development of Dry Plates.—Wet Collodion is developed by the simple application of a reducing agent to the surface of the film. In a dry process, however, the effect of pouring on a solution of Pyrogallic Acid alone would often be to obliterate the image instead of developing it, and thus to restore the plate again to a sensitive state (p. 51). The difference depends upon the fact that in the wet process you have free Nitrate of Silver in contact with the Iodide, but in the dry process this Nitrate has been washed away, and hence it is necessary to add it to the Pyrogallic Acid, which when used alone is not a developer in the proper sense of the term (p. 40).

Skilful Photographers find by experience that they are able to control the development of dry plates by varying the relative quantities of Nitrate of Silver and of the reducing agent. This proceeding is quite necessary, because the quality of the resulting Negative is much influenced by the length of the exposure in the Camera, and it constantly happens in a dry process that too much or too little exposure has been allowed. Under-exposure is favourable to excessive contrast in the Negative, some parts being highly opaque and others translucent. Over-exposure, on the other hand, produces too much uniformity, the half-tones and the high lights being nearly of the same depth. Now it is found that a developer containing a large relative proportion of Nitrate of Silver adds to the contrast between the tones, whilst, on the other hand, a diminished proportion of the same compound lessens the contrast. The Artist therefore keeps both solutions conveniently near at hand, and observes the behaviour of the image. If the light has acted for too short a time, and hence has failed in impressing the shadows decidedly, he compensates for the defect as far as possible by increasing the strength of his Pyrogallic Acid solution; whereas when he sees any evidence of over-action of light in the diminished intensity of the fully-exposed portions of the film, he then encourages a vigorous deposition of Silver by dropping in the Nitrate more freely.

An improved developer for dry processes has lately been devised by Major Russell. The modification consists in mixing the retarding acid with the Nitrate of Silver, instead of adding it to the reducing agent in the usual way. Supposing the balance between the Acid and the Silver to be properly adjusted, the developer will seldom become turbid, because if an excess of the Nitrate be inadvertently added to the solution of Pyrogallic Acid, a corresponding excess of Citric Acid will be introduced with it and will counteract the effect. The suggestion is one which has been found to possess a practical value, and to assist much in securing brilliancy and freedom from fogging.

Comparative Sensitiveness and keeping qualities of Dry Plates.—The comparative sensitiveness of wet and dry Collodion has been variously estimated at from four to forty times in favour of the former. The discrepancy depends partly upon the fact that the most sensitive variety of wet Collodion has rarely been employed in the experiments, and partly also upon the difference of opinion as to what constitutes a fully-exposed plate in dry Collodion Photography. If you take four pictures upon the same glass, and allow two, four, six, and eight minutes respectively in the Camera, there will be less difference between the resulting Photographs than might have been anticipated, the principal effect of the prolonged exposure appearing in the form of a few additional details in the shadows, and of a better and more harmonious Negative. Taking ordinary wet Collodion, as it is generally used, iodized with simple Iodides only, and supposing twenty seconds to be the correct time of exposure, the Writer would allow two minutes and a half for a dry plate preserved with Tannin. He has succeeded in making dry plates considerably more sensitive than here described, but not without losing in intensity; and when such is the case, the contrast and intensity of development being too much reduced, it will be found very difficult to prevent the high lights, such as the sky, from passing beyond their proper boundaries and encroaching upon the shadows. There will also be a want of sharpness and decision in the image under such circumstances, so that fine lines in the picture will coalesce, the space between them being obliterated by deposited Silver.

The keeping qualities of dry plates have also been variously stated. The Writer himself has not been successful with long kept plates, and has usually found spots during development, arising, as he supposes, from minute particles in the film having become centres of chemical action. After the plates have been exposed in the Camera, the chances of obtaining a perfect picture are still further diminished by long keeping, since the image will in some cases develope spontaneously, and in others will partially disappear so as not to admit of a perfect development.

GENERAL OBSERVATIONS ON DRY COLLODION PROCESSES.

a. *Different forms of Iodide of Silver.*—It was shown at page 130 that Iodide of Silver forms a crystalline compound with Nitrate of Silver, known as Iodo-Nitrate of Silver; the crystals of which are soluble without change in a concentrated solution of Nitrate of Silver, but are decomposed into free Iodide of Silver and free Nitrate of Silver by treatment with water. This Iodo-Nitrate of Silver, however, is not of much importance in Photography, for in the wet process, it exists in the film only in minute quantities, and in the dry process it is altogether absent, the plates being invariably washed in water before drying.

Iodide of Silver possesses another peculiarity, which is more important to the Photographer than its property of combining with Nitrate of Silver. We refer to its existence in two states, which may be designated by the terms sensitive and insensitive.

Sensitive Iodide of Silver is formed when a soluble Iodide is added to Nitrate of Silver, the latter salt being in excess. Insensitive Iodide is formed by the admixture of the same salts, but with the soluble Iodide in excess instead of the Nitrate. The two forms of Iodide differ from each other in colour and general appearance, the sensitive being of a greenish-yellow and rather dense, the insensitive nearly white and comparatively bulky: in chemical composition, however, they are believed to be the same, provided they have been thoroughly washed with distilled water to remove the precipitating salts left in excess.

Let us notice the conditions under which these two forms of Iodide are mutually convertible. The application of a solution of Iodide of Potassium or of any other soluble Iodide immediately renders the sensitive Iodide insensitive, and no amount of washing with water will restore to it the property of being impressed in the Camera. On the other hand, a solution of Nitrate of Silver imparts sensitiveness to the form of Iodide which lacks it, and although the excess of Nitrate be afterwards removed by abundant ablutions, sensitiveness still remains. Sensitive Iodide of Silver placed in contact with Chloride of Sodium and dried, either receives no impression at all in the Camera, or at all events an imperfect one; but if it be washed with water to remove the Chloride of Sodium, its sensitiveness is in a measure restored.

b. *Organic Compounds containing Iodide, Bromide, and Chloride of Silver.*—The study of this class of bodies is necessary to a perfect comprehension of the phenomena of dry Collodion. If the Albumen of an egg be added by degrees to the ordinary Photographic Nitrate Bath containing Iodide of Silver dissolved, the first addition causes a white precipitate, which is not simple Albuminate of Silver described at page 20, but a compound of Albuminate of Silver with Iodide of Silver. One property of this substance is that it is capable of existing in a perfectly transparent condition, in lumps resembling calf's-foot jelly or gelatinous silica: this we mention because it explains the cause of the pale opaline appearance of an excited Albumen film as compared with the opaque and creamy aspect of a Collodion film.

Glycyrrhizine, or Sugar of Liquorice, added to the Photographic Bath in small quantity throws down a yellow precipitate of Glycyrrhizinate of Silver with Iodide of Silver. This substance has a strong acid reaction, the Glycyrrhizine having united with the

Oxide of Silver and displaced the Nitric Acid. When treated with Ammonia it behaves in a manner quite peculiar: the whole deposit appears at once to dissolve, yet on close examination it is seen that the solution is not complete, but that the liquid contains suspended matter in a form nearly invisible. Bearing this in mind, we comprehend the phenomena produced by adding Glycyrrhizine to Collodion, for it is found that if this addition be carried beyond a certain limited point, the film will remain perfectly clear on dipping it in the Bath, and will exhibit no deposit visible to the eye.

Gelatine combines with Nitrate of Silver, and the combination again unites with Iodide of Silver. The substance so formed is soluble to a certain extent in a solution of the Gelatino-Nitrate of Silver, and no precipitation of Iodide of Silver is produced by dilution with water. If however the solution be boiled with a little free Nitric Acid in order to decompose the organic compound, then the Iodide will be thrown down in a milky state. The above explains the reason that commercial Gelatine, although nearly always containing common Salt, seldom gives any precipitate with Nitrate of Silver: it will be sufficient in such a case to acidify with a few drops of Nitric Acid and heat to 212° Fahr., to obtain a decided turbidity. We have spoken already of combinations of Iodide of Silver with Nitrate of Silver, and shown that corresponding compounds of Bromide and Chloride with Nitrate of Silver cannot be formed. Bromide of Silver and Chloride of Silver however surpass the Iodide of Silver in affinity for the organic compounds of Silver, and it will be instructive to examine two or three of the more remarkable of the properties of the combinations so produced.—

Chloride of Silver is insoluble in water, and comparatively so in a strong solution of Nitrate of Silver. When however Nitrate of Silver is mixed with organic matter, an appreciable quantity of Chloride will be dissolved by it. Hence it follows that in washing a Collodion film, after taking it from the Bath, a solution of common Salt cannot be depended on as a test to show when the whole of the Nitrate of Silver has been removed. The washings from such a plate may give no immediate precipitate with Salt, and may yet contain enough Nitrate of Silver to have a distinctly bitter and metallic taste.

We gain a correct notion of the relative affinities of Iodide, Bromide, and Chloride of Silver for organic compounds of Silver, by selecting a plain Collodion, the Pyroxyline of which is so prepared as to possess a portion of what we term the organic reactions, and by dissolving in it separately an Iodide, a Bromide, and a Chloride: on coating glasses with these Collodions and dipping in the Bath, the first will produce a yellow film, the second a pale opaline-blue film, and the third will remain clear, exhibiting no precipitate whatever upon the glass. Unless the experiments of the Author have led him to erroneous conclusions, this gradual diminution of opacity is a measure of the extent to which the affinity reaches.

Observe the importance of remembering the preceding reactions in experimenting with dry Collodion. Free Iodide of Potassium has been shown to convert the sensitive form of Iodide of Silver into the insensitive, and this in so complete a manner that the sensitiveness cannot be restored by washing with water. It is possible however to apply Iodide of Potassium to a Collodion film, and yet afterwards to succeed in obtaining a feeble picture, if the excess of Iodide be perfectly removed by hot water: the explanation probably is that the Collodion film is not simply an Iodide of Silver, but contains a portion of an organic compound not immediately decomposable by Iodide of Potassium. Suppose again that a film of sensitive Iodide of Silver with a trace of Nitrate of Silver adhering to it be washed with Iodide of Potassium dissolved in Albumen. The sensitiveness will be destroyed thereby, as long as the excess of Iodide of Potassium remains upon the film, but it will return in a measure on washing the film with water, because a portion of the Albuminate of Silver remains undecomposed. The affinity of Albumen for Nitrate of Silver appears to be very great. When an Iodide and a Chloride exist together in aqueous solution, and a *limited* amount of Nitrate of Silver is added, the Iodide appropriates it to the exclusion of the Chloride. But when Albumen is mixed with an Iodide, the most careful addition of Nitrate of Silver will throw down a compound precipitate from the very first.

Organic matter of certain kinds present in the Nitrate Bath will modify the Photographic properties of a film excited in that Bath. For just as an organic body withdraws in insoluble combination Iodide of Silver from its solution in Nitrate of Silver, so conversely does Iodide of Silver in falling carry down with it traces of organic matters previously dissolved in Nitrate of Silver; whilst Bromide of Silver and Chloride of Silver effect the same in a manner still more decided. The precipitate formed when Chloride is added to Nitrate of Silver previously mixed with organic matter is often in a state of excessively fine division, so that it occupies a long time in subsiding. On analysis it appears that the organic matter is present in very small quantity, scarcely more than what the chemist would term "a trace," yet the action of light is much controlled by it, and we find that the Chloride of Silver thrown down from a solution of Nitrate of Silver containing a little Gelatine always darkens in the sun to a brick-red instead of the usual violet-blue. The Iodide of Silver also which is precipitated in a Bath containing certain organic matters, gives, even in a Preservative process, a Negative image with greater contrast, and one which developes more quickly than usual.

c. *Manufacture of Collodion for the Dry Processes.*—Much that it would otherwise have been necessary to describe under this head, has been already given in the Sixth Chapter, page 105. We require in dry Collodion certain physical qualities, such as adhesiveness to the glass, and a moderate amount of porosity. Preservative organic bodies tend to loosen the film from the glass, and hence the necessity of making the Collodion as adherent as possible. In effecting this, attention must be paid to the temperature of the acids, which ought not to be under 150° Fahr., and may sometimes with advantage be raised to 160° Fahr. Hot acids disintegrate Pyroxyline and render it short and friable, whereas cold acids give a strong and tough film, which leaves the glass in a connected skin. Secondly, a considerable quantity of water must be used in the Nitrosulphuric Acid, because this assists in breaking up the structure of the Pyroxyline and in rendering it adhesive.

Here we pause to make an observation which is important as regards Collodion for dry processes. It has been shown that the fibre of the Pyroxyline must be considerably broken up to ensure an adhesive Collodion, and that high temperature and abundance of water in the acids are both favourable. Now in effecting the object proposed, it will be proper to avail ourselves of both conditions, and not to trust too much to the latter, for it is found that a high temperature increases the intensity of the Collodion, whereas a dilution of the acids lessens it. Collodions have been made with which it is difficult to succeed in obtaining opaque skies to landscapes, in consequence of the Nitrosulphuric Acid having been mixed with too large a quantity of water. You may often recognize such Collodions by their requiring an unusually long time to set upon the glass, the reason of which is explained at page 108. To obviate the occurrence of this difficulty, it is advised that the Nitrosulphuric Acid should contain at least *two measures* of Oil of Vitriol to one of Nitric Acid of 1·45 sp. gr., and that the temperature should be maintained steadily at 160° Fahr. No fear need then be entertained of the water being in excess, because the immediate effect of making the acids too weak in that formula would be to dissolve the whole of the Pyroxyline. If however equal bulks of Oil of Vitriol and Nitric Acid were used with the maximum of water, and the temperature allowed to fall to 140° Fahr., you might obtain a Pyroxyline, apparently disintegrated to the correct point, and also one giving a porous and adhesive film, but the Collodion would produce an excessively feeble Negative, unless free Nitrate of Silver were left upon the film, in addition to the organic preservative.

Although a difference of opinion exists as to whether Negative Collodion for the wet process ought to be simply iodized or bromo-iodized, all are agreed that Collodion for the dry process should contain a portion of Bromide. The Writer has before shown (p. 53) that the effect of Bromide in Collodion varies with the presence or absence of organic matter. An affinity exists between Bromide of Silver and organic matters coagulated by Nitrate of Silver, and this affinity is more marked than that between *Iodide* of Silver and organic matters coagulated in the same way; hence we find that Bromide of Silver in a dry process interferes neither with the rapidity nor with the intensity of the development, but often increases both. The dry process is also peculiar as regards the increased length of exposure given in the Camera, and hence we have an additional reason for dismissing from our minds all preconceived ideas as to the action of Bromide, derived from the use of that substance in the ordinary wet Collodion process.

Collodion for the dry processes should always contain a sufficiency of Iodide to produce an opaque film in the Bath, since solarization or over-action of light in the sky is more marked when the film is transparent. Mr. Moxham has shown that in such a case the actinic rays, after acting for a certain time, pass through the film, and may be received on a second plate placed behind it: this observation is very important.

In Collodion for the dry processes we are accustomed to rely much upon changes produced by iodizing with an alkaline Iodide and subsequent keeping, which have been shown at pages 126 and 127, to result in the formation of Nitrite, and also of an organic substance which combines with Nitrate of Silver; the adhesiveness and porosity of the Collodion being at the same time augmented. At present we need only indicate the propriety of bearing these changes in mind and making allowance for them at the time of manufacturing the Collodion. For example, it would be possible to prepare a Pyroxyline so hard and contractile as to be quite unsuitable, and yet to bring the Collodion at once into the proper state by agitating it with powdered Carbonate of Potash until liquefaction was produced. Conversely, the temperature and degree of dilution of the acids might be so adjusted as to render the Pyroxyline independent of any assistance from decomposition after iodizing. Far better however would be an intermediate method, in which the newly iodized Collodion was purposely left a little deficient in porosity, and then kept for a time in the iodized condition, to bring it exactly into the proper state.

Old Linen rags, or paper from the same, have been used for dry Collodion. The Author sums up his experience of such materials as follows:—They produce a Pyroxyline very adhesive and porous, and with stronger organic reactions than that from Cotton. This Pyroxyline is however unstable both before and after iodizing, and although giving great intensity, often fails in yielding the details of foliage and other dark objects. If any should adopt the use of Linen Pyroxyline, let it be remembered, that the proportion and strength of the acids, the temperature, the relative bulks of Alcohol and Ether, the nature of the Iodide, etc., must all be varied from the usual formulæ.

Dry Collodion may be made porous by other methods not yet described. Mr. Hockin* has shown that Iodoform will destroy the parchment quality common in recently prepared Collodion; and even if we add no extraneous substance whatever, we find as a rule that plain Collodion becomes more porous by simple keeping, especially when made from Methylated Ether (p. 121).

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* 'Practical Hints on Photography, its Chemistry and its Manipulations,' third edition, p. 75.

CHAPTER X.

ON THE THEORY OF THE DAGUERREOTYPE AND TALBOTYPE PROCESSES, ETC.

SECTION I.

The Daguerreotype.

It was not the original intention of the Author to include a description of the Daguerreotype Process within the limits of the present Work. The Daguerreotype is a branch of the Photographic Art so distinct from the others, that, in manipulatory details, it bears very little analogy to them; a slight sketch of the theory of the process may not however be unacceptable.

All necessary remarks will fall under three heads:—The preparation of the Daguerreotype film; the means by which the latent image is developed; and the strengthening of the image by the Hyposulphite of Gold.

The Preparation of the Daguerreotype Film.—The sensitive film of the Daguerreotypist is in many respects different from that of the Calotype or Collodiotype. The latter may be termed *wet processes,* in contradistinction to the former, where aqueous solutions are not employed. The Daguerreotype film is a pure and isolated Iodide of Silver, formed by the direct action of Iodine upon the metal, and it is important to remember that Iodide of Silver so prepared is different in its Photographic action from the yellow salt obtained by double decomposition between Iodide of Potassium and Nitrate of Silver. A Daguerreotype film, when exposed to a bright light, first darkens to an ash-grey colour and then becomes nearly white; the solubility in Hyposulphite of Soda being at the same time lessened. A Collodion film, on the other hand, if the excess of Nitrate of Silver be washed off, although still capable of receiving the radiant impression in the Camera, does not alter either in colour or in solubility by exposure to the sun's rays.

Details of the progress for preparing a Daguerreotype Plate.—A copper plate of moderate thickness is coated upon the surface with a layer of pure Silver, either by the electrotype or in any other convenient manner. It is then polished with great care, until the surface assumes a brilliant metallic lustre. This preliminary operation of polishing is one of great practical importance, and the troublesome details attending it constitute one of the main difficulties to be overcome.

After the polishing is complete, the plate is ready to receive the sensitive coating. This part of the process is conducted in a peculiar manner. A simple piece of cardboard or a thin sheet of wood, previously soaked in solution of Iodine, evolves enough of the vapour to attack the silver plate; which being placed immediately above, and allowed to remain for a short time, acquires a pale-violet hue, due to the formation of *an excessively delicate layer* of Iodide of Silver. By prolonging the action of the Iodine the violet tint disappears and a variety of prismatic colours are produced, much in the same way as when light is decomposed by thin plates of mica or the surface of mother-of-pearl. From violet the plate becomes of a straw-yellow, then rose-colour, and afterwards steel-grey. As the Iodine acts further, this sequence of tints is repeated; the steel-grey disappears, and the yellow and rose-colours recur. The deposit of Iodide of Silver gradually increases in thickness during these changes; but to the end it remains excessively thin and delicate. In this respect it contrasts strongly with the dense and creamy layer often employed in the Collodion process, and shows that a large proportion of the Iodide of Silver must in such a case be superfluous, as far as any influence produced by the light is concerned. An inspection of a sensitive Daguerreotype plate reveals the *microscopic* nature of the actinic changes involved in the Photographic Art, and teaches a useful lesson.

Increase of sensibility obtained by combining the joint action of Bromine and Iodine.—The original process of Daguerre was conducted with the vapour of Iodine only; but in the year 1840 it was discovered by Mr. John Goddard that the sensibility of the plate was greatly promoted by exposing it to the vapours of Iodine and Bromine in succession,—the proper time for each being regulated by the tints assumed.

The composition of this *Bromo-Iodide* of Silver, so called, is uncertain, and has not been proved to bear any analogy to that of the mixed salt obtained by decomposing a solution of Iodide and Bromide of Potassium with Nitrate of Silver. Observe also that the Bromo-Iodide of Silver is more sensitive than the simple Iodide *only when the vapour of Mercury is employed as a developer.* M. Claudet proves that if the image be formed by the direct action of light alone (see next page) the usual condition is reversed, and that the use of Bromide under such circumstances retards the effect.

The development and properties of the Image.—The latent image of the Daguerreotype is developed in a manner different from that of the humid processes generally,—viz. by the action of Mercurial vapour. The cup containing the Quicksilver is previously heated by means of a spirit-lamp to about 140° Fahrenheit: although the amount of Mercurial vapour evolved at this temperature is very small, it is sufficient for the purpose, and after continuing the action for a short time the image is perfectly developed.

There are few questions which have given rise to greater discussion amongst chemists than the nature of the Daguerreotype image. Unfortunately, the quantity of material to be operated on is so small, that it becomes almost impossible to ascertain its composition by direct analysis. Some suppose it to consist of Mercury alone. Others have thought that the Mercury is in combination with metallic Silver. The presence of the former metal is certain, since M. Claudet shows that, by the application of a strong heat, it can actually be volatilized from the image in sufficient quantity to develope a second impression immediately superimposed.

It is a remarkable fact that an image more or less resembling that developed by Mercury can be obtained by *the prolonged action* of light alone upon the iodized plate. The substance so formed is a white powder, insoluble in solution of Hyposulphite of Soda; amorphous to the eye, but presenting the appearance of minute reflecting crystals when highly magnified. Its composition is uncertain.

For all practical purposes the production of the Daguerreotype image by light alone is useless, on account of the length of time required to effect it. This was alluded to in the Third Chapter, where it was shown that in the case of the Bromo-Iodide of Silver an intensity of light 3000 times greater would be required, if the use of the Mercurial vapour were omitted.

M. Ed. Becquerel's discovery of the continuing action of rays of yellow light.—Pure homogeneous yellow light has no action upon the Daguerreotype plate; but if the iodized surface be first exposed to white light for a sufficient time to impress a latent image, and then *afterwards* to the yellow light, the action already commenced is *continued*, and even to the extent of forming the peculiar white deposit, insoluble in Hyposulphite of Soda, already alluded to.

Yellow light may therefore in one sense be spoken of as a *developing* agent, since it produces the same effect as the Mercurial vapour in bringing out to view the latent image.

A singular anomaly however requires notice, viz. that if the plate be prepared with the mixed vapours of Bromine and Iodine, in place of Iodine alone, then the yellow light cannot be made to develope the image. In fact, the same coloured ray which continues the action of white light upon a surface of Iodide of Silver, actually *destroys* it, and restores the particles to their original condition, with a surface of Bromo-Iodide of Silver.

These facts, although not of great practical importance, are interesting in illustration of the delicate and complex nature of the chemical changes produced by light.

The Strengthening of the Daguerreotype Image by means of Hyposulphite of Gold.—The use of the Hyposulphite of Gold to whiten the Daguerreotype image, and render it more lasting and indestructible, was introduced by M. Fizeau, subsequent to the original discovery of the process.

After removal of the unaltered Iodide of Silver by means of Hyposulphite of Soda, the plate is placed upon a levelling-stand and covered with a solution of Hyposulphite of Gold, containing about one part of the salt dissolved in 500 parts of water. The flame of a spirit-lamp is then applied until the liquid begins to boil. Shortly a change is seen to take place in the appearance of the image; it becomes whiter than before, and acquires great force. This fact seems to prove conclusively that metallic Mercury enters into its composition, since a surface of Silver—such, for instance, as that of the Collodion image—is *darkened* by Hyposulphite of Gold.

The difference in the action of the gilding solution upon the image and the pure Silver surrounding it illustrates the same fact. This Silver, which appears of a dark colour and forms the shadows of the image, is rendered still darker; a very delicate crust of metallic Gold *gradually* forms upon it, whereas in the case of the image itself the whitening effect is immediate and striking.

SECTION II.

Theory of the Talbotype and Albumen Processes.

The Talbotype or Calotype.—This process, as practised at the present time, is almost identical with that originally described by Mr. Fox Talbot. The object is to obtain an even and finely divided layer of Iodide of Silver upon the surface of a sheet of paper; the particles of the Iodide being left in contact with an excess of Nitrate of Silver, and usually with a small proportion of Gallic Acid.

The English papers sized with Gelatine are commonly used for the Calotype process: they retain the film more perfectly at the surface, and the Gelatine in all probability assists in forming the image. With a foreign starch-paper, unless it be re-sized with some organic substance, the solutions sink in too deeply, and the picture is wanting in clearness and definition.

There are two modes of iodizing and sensitizing the sheets: first, by floating alternately upon Iodide of Potassium and Nitrate of Silver, in the same manner as in the preparation of papers for Positive Printing; and second, by what is termed "the single wash," which is thought by many to give superior results as regards sensitiveness and intensity of image. To iodize by this mode, the yellow Iodide of Silver, prepared by mixing solutions of Iodide of Potassium and Nitrate of Silver, is dissolved in a *strong* solution of Iodide of Potassium; the sheets are floated for an instant upon this liquid and dried; they are then removed to a dish of water, by the action of which the Iodide of Silver is precipitated upon the surface of the paper in a finely divided state.

The properties of a solution of Iodide of Silver in Iodide of Potassium, or of the double Iodide of Potassium and Silver, are described at page 56, a reference to which will show that the double salt is *decomposed* by a large quantity of water, with precipitation of the Iodide of Silver, this substance being less soluble in a *dilute* solution of Iodide of Potassium than in a strong solution.

Paper coated with Iodide of Silver by this mode, after proper washing in water to remove soluble salts, will keep good for a long time. The layer of Iodide appears of a pale primrose-colour, and is *perfectly insensitive to light*, so that exposure to the sun's rays produces no change.

To render Calotype paper sensitive to light, it is brushed with a solution of Nitrate of Silver containing both Acetic and Gallic Acid, termed "Aceto-Nitrate" and "Gallo-Nitrate" solution. The Gallic Acid lessens the keeping qualities of the paper, but increases the sensitiveness. The Acetic Acid prevents the paper from blackening all over during the development, and preserves the clearness of the white parts; its employment is indispensable.

The paper is commonly excited upon the morning of the day upon which it is intended to be used; and the longer it is kept, the less active and certain it becomes. An exposure of five to eight minutes in the Camera is the average time with an ordinary view Lens.

The picture is developed with a saturated solution of Gallic Acid to which a portion of Aceto-Nitrate of Silver has been added to heighten the intensity. Both Sulphate of Iron and Pyrogallic Acid have also been used, but the gradual action of a more feeble developer is preferable in this process.

After fixing the Negative by removing the unaltered Iodide of Silver with Hyposulphite of Soda, it is well washed and dried. White wax is then melted in with a hot iron so as to render the paper transparent, and to facilitate the after-process of printing.

The Calotype cannot be compared with the Collodion process for sensitiveness and delicacy of detail, but it possesses advantages for tourists and those who do not wish to be encumbered with large glass plates. The principal difficulty appears to be in obtaining a uniformly good paper, many samples giving a speckled appearance in the black parts of the Negative.

The Waxed Paper process of Le Grey.—This is a useful modification of the Talbotype, introduced by M. Le Grey. The paper is waxed *before iodizing*, by which, without involving any additional operation, a very fine surface layer of Iodide of Silver can be obtained. The Waxed Paper Process is well adapted for tourists, from its extreme simplicity and the length of time which the film may be kept in a sensitive condition.

Both English and foreign papers are employed: but the former take the wax with difficulty. Mr. Crookes, who has devoted his attention to this process, gives clear directions for waxing paper; it is essential that pure white wax should be obtained direct from the bleachers, since the flat cakes sold in the shops are commonly adulterated. The *temperature* must also be carefully kept below that point at which decomposition of the wax takes place; the use of too hot an iron being a common source of failure (see 'Photographic Journal,' vol. ii. p. 231).

The sheets of paper, having been properly waxed, are soaked for *two hours* in a solution containing Iodide and Bromide of Potassium, with enough free Iodine to tinge the liquid of a port-wine colour. The greasy nature of wax impedes the entry of liquids, and hence a long immersion is required. The iodizing formulæ of the French Photographers have been encumbered by the addition of a variety of substances which appear to introduce complications without giving proportional advantage, and it is now known that the Iodide and Bromide of Potassium, with free Iodine, are sufficient. This latter ingredient was first used by Mr. Crookes: it seems to add to the clearness and sharpness of the Negatives; and as the papers are *coloured* by the Iodine, air-bubbles cannot escape detection. The process of exciting with Nitrate of Silver is also rendered more certain by the employment of free Iodine, the action of the Bath being continued until the purple colour gives place to the characteristic yellow tint of the Iodide of Silver.*

Waxed Paper is rendered sensitive by immersion in a Bath of Nitrate of Silver containing Acetic Acid; the quantity of which latter ingredient should be increased when the papers are to be long kept. As the excess of Nitrate is subsequently removed, the solution may be used weaker than in the Calotype or Collodion process.

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* The later experience of the Writer induces him to believe *that organic matter* may be used with advantage in the waxed paper process, and that serum of milk is a better vehicle for the chemicals than pure water.

After exciting, the papers are washed with water to reduce the amount of free Nitrate of Silver to a minimum. This lessens the sensitiveness, but greatly increases the keeping qualities, and the paper will often remain good for ten days or longer.

It is a very important point, in operating with Waxed Paper, to keep the developing dishes clean. The development is conducted by immersion in a Bath of Gallic Acid containing Acetic Acid and Nitrate of Silver; and being retarded by the superficial coating of wax, there is always a tendency to an irregular reduction of Silver upon the white portions of the Negative. When the developer becomes brown and discoloured, this is more likely to happen; and it is well known to chemists that the length of time during which Gallic Acid and Nitrate of Silver may remain mixed without decomposing, is lessened by using vessels which are dirty from having been before employed for a similar purpose. The black deposit of Silver exercises a *catalytic* action (*καταλυσις*, decomposition by contact) upon the freshly-mixed portion, and hastens its discoloration.

The Waxed Paper process is exceedingly simple and inexpensive,—very suitable for tourists, as requiring but little experience, and a minimum of apparatus. It is, however, tedious in all its stages, the sensitive papers frequently taking an exposure of twenty minutes in the Camera, and the development extending over an hour or an hour and a half. Several Negatives, however, may be developed at the same time; and as the removal of the free Nitrate of Silver gives the process a great advantage during hot weather, it will in all probability continue to be followed. The prints which have been sent to the exhibition of the Photographic Society, show that waxed paper in the hands of a skilful operator may be made to delineate architectural subjects with great fidelity, and also to give the details of foliage and landscape Photography with tolerable distinctness.

The Albumen process upon Glass.—The process with

Albumen originated in a desire to obtain a more even surface layer of Iodide of Silver than the coarse structure of the tissue of paper will allow. It is conducted with simple Albumen, or "white of eggs," diluted with a convenient quantity of water. In this glutinous liquid Iodide of Potassium is dissolved: and the solution, having been thoroughly shaken, is set aside, the upper portion being drawn off for use, in the same manner as in the preparation of Albuminized paper for printing.

The glasses are coated with the iodized Albumen, and are then placed horizontally in a box to dry. This part of the process is considered the most troublesome, the moist Albumen easily attracting particles of dust, and being apt to blister and separate from the glass. If an even layer of the dried and Iodized material can be obtained, the chief difficulty of the process has been overcome.

The plates are rendered sensitive by immersion in a Bath of Nitrate of Silver with Acetic Acid added, and are then washed in water and dried. They may be kept for a long time in an excited state.

The exposure in the Camera must be unusually long; the free Nitrate of Silver having been removed by washing, and the Albumen exercising a direct retarding influence upon the sensitiveness of Iodide of Silver (p. 45).

The development is conducted in the ordinary way by a mixture of Gallic Acid and Nitrate of Silver, with Acetic Acid added to preserve the clearness of the lights. It usually requires one hour or more, but may be accelerated by the gentle application of heat.

Albumen pictures are remarkable for elaborate distinctness, and are admirably adapted for viewing in the Stereoscope; but they do not often possess the peculiar and characteristic *softness* of the Photograph upon Collodion. The process is well adapted for hot climates, being very little prone to the cloudiness and irregular reduction of Silver which are often complained of with moist Collodion under such circumstances.

Amateurs practising the Albumen process for the first time are often surprised at the *pale transparent appearance* of the plates on being raised from the Nitrate Bath, giving the idea that too little Iodide of Potassium had been used. This peculiarity, however, depends upon *the chemical nature* of the Albumen itself. It has an affinity for Iodide of Silver, and unites with it, producing a film of a different character from the Collodio-Iodide of Silver. *Glycyrrhizine*, the sugar of Liquorice, added in excess to Collodion, diminishes the opacity of the sensitive film in a similar manner, by uniting chemically with the Iodide of Silver.

SECTION III.

Photographic Processes by Sir John Herschel and others.

Under this head may be included the processes known by the name of Cyanotype, Chrysotype, etc., together with the Photo-galvanographic, Photo-lithographic, Photo-glyphic, and Carbon Printing Processes, all of which involve chemical reactions of the greatest interest.

Processes with Persalts of Iron.—Sir John Herschel discovered, about 1840, that certain of the Persalts of Iron when exposed to sunlight in contact with organic matter, were reduced to the state of Protosalts. The Perchloride of Iron has this property when accurately neutralized, but the Ammonio-Tartrate and Potassio-Tartrate of Iron are more easily affected by light, whilst the Ammonio-Citrate is sensitive to a degree greater than either. All these processes are slower than the ordinary modes of printing in which the Chloride of Silver is employed.

In the manipulations, a sheet of photographic pape ris brushed with a solution of the yellow Persalt, and when dry placed in the sun in the usual way. The image so formed is always faint, but it may be intensified by either of the following methods :—

a. *By the Ferridcyanide of Potassium.*—This process was named by the inventor, the "Cyanotype." Ferridcyanide of Potassium, also known as "Red Prussiate of

Potash," produces no precipitate with the Persalts of Iron, but throws down a variety of Prussian blue (Turnbull's blue) when added to the Protosalts. Consequently on treating the Iron-print with a solution of Ferridcyanide of Potassium, those parts which have been sunned, and thereby reduced to the lower form of oxide, assume a blue tint.*

b. *Intensifying by Chloride of Gold.*—When this plan of intensifying the image on the Ammonio-Citrate paper is adopted, the inventor terms the process "Chrysotype" (from *χρυσος, gold*). The image must be exposed for a brief time only and should be very faint. On brushing it with a dilute neutral solution of Chloride of Gold, the Protosalt of Iron on the parts touched by light, tending to reabsorb the oxygen of which it had previously been deprived, reduces the Gold, and a purple image is the result; this image continues to darken by precipitation of fresh particles until it is nearly black.

c. *Intensifying by other Metallic Compounds admitting of Deoxidation.*—Nitrate of Silver, when applied to the image, is slowly reduced, and darkens the tone considerably. Proto-Nitrate of Mercury acts in the same way, but pictures containing Mercury or its Oxide are liable to fade. Bichromate of Potash placed in contact with those parts of the Ammonio-Citrate paper which have been sunned, likewise gives up Oxygen and is precipitated upon the image in the form of a lower oxide of Chromium.

Processes with Salts of Uranium.—Mr. Burnett, following in the steps of Sir John Herschel, ascertained that the Persalts of Uranium had similar Photographic properties to the Persalts of Iron, and were reduced to Protosalts by light and organic matter acting conjointly.

Uranium is a rare metal, forming a coloured series of salts somewhat analogous in composition to the Proto- and

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* In place of the Ferridcyanide, the Ferrocyanide of Potassium, known as yellow Prussiate of Potash, may be employed, if the prints are afterwards thrown into water. The reaction, however, is not so simple, since the Ferrocyanide of Potassium forms a *white* precipitate with Protosalts of Iron, which becomes blue by oxidation. With unchanged Ammonio-Citrate of Iron, Ferrocyanide of Potassium produces no precipitation.

Persalts of Iron. Paper saturated with a solution of the *Pernitrate* of Uranium, a salt always obtainable in commerce, receives a very distinct image on exposure to light, which may be further intensified either by Chloride of Gold or Nitrate of Silver, as above described. In either case the Uranium compound, previously reduced under the influence of light, re-absorbs Oxygen, and the noble metal is in consequence precipitated upon the image. The colour of these prints is better than those produced by Sir John Herschel's process above described, and may be further improved by different processes of toning.

Processes with Bichromate of Potash.—These are the invention of Mr. Mungo Ponton, and were first announced some years since in the 'Edinburgh New Philosophical Journal.'

Bichromate of Potash contains Chromic Acid, a yellow crystalline body, which is a high Oxide of the metal Chromium. Light alone produces no effect upon Chromic Acid, but if organic substances are also present, the Chromic Acid is reduced to the condition of a lower Oxide of Chromium, and the liberated Oxygen unites with the organic body. Some kinds of organic matter act more decidedly than others, and especially *Gelatine*, which reduces the Bichromate rapidly in presence of sunlight; the Gelatine itself being oxidized into a resinous substance, which remains in union with Oxide of Chromium.

The image obtained upon gelatinized paper soaked in Bichromate of Potash is of a tawny colour, and not very vigorous, but Mr. Hunt and others succeeded in getting a better effect by associating certain coloured salts, such as those of Copper and Nickel, with the Bichromate, and afterwards toning with Nitrate of Silver, etc. The Chromates of many of the metals are most brilliant in colour, and quite equal in that respect to the Ferrocyanides and Ferridcyanides before alluded to.

Another mode of toning Photographic prints prepared by the above method, has been described by Mr. Perry, and also by M. Sella, of Piedmont. The pictures, after having been washed in water to remove the unaltered Bichromate, are immersed in a solution of Sulphate of Iron. They are then washed a second time in water, and treated with Gallic or Pyrogallic Acid, the effect of which is to change the shadows to a bluish-black colour, having a composition similar to common writing-ink. This process depends upon the image retaining the Salt of Iron, so that when once applied it cannot afterwards be removed by washing with water.

CARBON PRINTING, PHOTO-LITHOGRAPHY, PHOTO-GALVANOGRAPHY, AND PHOTOGLYPHY.

In all these processes the peculiar Photographic properties of the Bichromate of Potash, before mentioned as the discovery of Mungo Ponton, are turned to account.

Carbon Printing.—M. Poitevin patented this process in 1855. Finely-divided charcoal is mixed with solutions of Bichromate of Potash and Gum Arabic, and dabbed on a sheet of paper. The Photographic impression is produced upon this surface by the action of light passing through a Negative picture, and the sheet is then washed with a sponge and a large quantity of water. The organic matter having been rendered insoluble by the light, the colour remains upon the sunned parts; but from the other portions of the paper, not touched by light, it is removed by the washing, leaving the surface white. The Oxide of Chromium, which is the product of Bichromate of Potash reduced by organic matter, is a mordant substance, having affinity for colours. Hence pigments of various kinds may be successfully employed in this process, and will remain fixed upon the image.

M. Testud de Beauregard proposed what he considered as an improvement on the above method, by applying only the Gum and Bichromate in the first instance, and putting on the Carbon when the paper had become dry. The process, however, although not at present patented, has never come into general use, because the delicacy and gradation of tone are not equal to that given by the ordinary Silver printing on albuminized paper. For the delineation of maps and line-engraving the Carbon printing is more suitable, but even here it has been superseded by the Photo-lithographic methods now to be described.

Photo-lithography.—In ordinary lithographic printing an absorbent stone is drawn upon with chalks purposely made of a waxy or fatty nature. The stone is then damped, so as to fill its pores with water in the parts not covered with drawing. A greasy ink is next laid on, which adheres to the waxy drawing, but is repelled by the watery surface of the stone. M. Poitevin patented a process in 1856, in which the required waxy or resinous design was produced by Photography in the following manner:—A stone covered with a layer of Bichromate of Potash and Gum, or Gelatine, was exposed to a luminous image, and then wetted with water. The parts acted on by light were found to have become greasy or resinous, and to refuse the water, so that the lithographic ink, afterwards applied, attached itself to them in preference to the moistened shadows.

The defects of M. Poitevin's process were, that if he exposed in the Camera, or under a transparent Positive, a *Negative* picture was produced on the stone. If, on the other hand, he exposed under a Negative, the picture, although Positive, was necessarily reversed, right-hand objects being on the left side, and *vice versâ.* In addition to these defects there were others relating to matters of practical detail, and hence the patent was eventually allowed to lapse.

In November, 1859, Mr. Osborne communicated a paper to the Melbourne Institute, on a Photo-lithographic process differing from that of M. Poitevin in some important particulars. The Bichromate of Potash and Gelatine were applied to *paper* in the first instance, and the image subsequently transferred to the stone: the objection of "reversed Positives" was thus removed, and other advantages were secured to the lithographer. Another peculiarity of Mr. Osborne's method is in his mode of inking. He does not begin by wetting the surface to make the unaltered Gelatine refuse the ink, but first inks-in the whole of the Photographic print, and then, by a subsequent washing process, removes the Gelatine from the unchanged parts after the manner described under the head of Carbon printing. The specimens exhibited prove that the process is perfect as far as reproducing black and white objects is concerned, but the inventor does not consider it to be equal to the ordinary silver printing in rendering light and shade by means of half-tints.

M. Asser, of Amsterdam, was an independent discoverer of a method which, in its essential features, resembles that of Mr. Osborne. In the early part of the year 1860 this method was adopted in the Ordnance Survey Department at Southampton, and improved in many of its minor details. The Photograph, as before, is made on paper, and transferred to a surface of zinc or stone. The ink is applied to the whole surface of the sheet of paper, in quantity more or less according to the boldness or fineness of the subject, and the unchanged parts are afterwards cleaned with a sponge. The method of transferring to Zinc varies according to the quantity of ink in the Photograph. Supposing this to be small, the "anastatic" process is adopted, in which the surface of the Zinc is slightly roughened by dilute Nitric Acid, and the drawing made to adhere to it by passing through a press: but when a larger quantity of ink was used, the Zinc is simply grained by rubbing with fine wet sand and a muller. In either case the prominence of the lines is further increased by acting on the interspaces with a very weak etching liquid, consisting of dilute Phosphoric Acid in Gum Water.*

Photo-galvanography, introduced into this country by Herr Pretsch, of Vienna, is a mode of producing, from a Photograph, an electrotype Copperplate in a state fit for printing. A glass is first coated with a mixture of Bichromate of Potash and Gelatine, other ingredients, not essential to the theory, being at the same time added for the purpose of giving what artists term "a grain." An image is next impressed upon this surface by the action of light. The object of the engraver is to make from the image *a surface partly raised and partly depressed*, such as would be required for carrying the printer's ink, and this is done by simply pouring water over the film. A characteristic property of Gelatine is to swell up by imbibing water, but Gelatine which has been altered in composition by light and Bichromate of Potash loses this property. Hence when water is applied to the film, those parts on which the light has *not* acted swell, but those on which it *has* acted remain as before: consequently the image becomes sunk in, and assumes the state required. It remains therefore only to make a gutta-percha mould of the image, to render that mould conducting by means of Carbon powder, and to deposit Copper upon it by the electrotype to any required thickness. The Copperplate so obtained is used for printing in the ordinary way.

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* The 'Report of the Progress of the Ordnance Survey,' published by Messrs. Eyre and Spottiswoode at her Majesty's Stationery Office, London, price 3*s*., by post 3*s*. 2*d*., contains a specimen of the results obtained by the Photo-zincographic process.

Photo-glyphy.—Mr. Fox Talbot has invented a mode of biting a Photograph into a steel plate. The Photographic impression is made upon a surface of Bichromate of Potash and Gelatine, as before. At first it was thought necessary to wash the plate afterwards in hot water, so as to dissolve away the unaltered Gelatine, and expose the bare surface of the metal. Subsequently, however, Mr. Talbot found that the removal of the unchanged parts of the film was not required, but that an aqueous solution of Perchloride of Iron would penetrate them and bite into the steel beneath. The Gelatine altered by light, however, does not absorb the aqueous liquid, but repels it, thus protecting the metal from the action of the solvent. It is very important that the etching liquid should be exactly of a certain strength, since a dilute solution of Perchloride of Iron soaks into a film of Gelatine more readily than a strong solution.

PART II.

PRACTICAL DETAILS OF THE COLLODION PROCESS.

PRACTICAL DETAILS OF THE COLLODION PROCESS.

CHAPTER I.

PHOTOGRAPHIC CHEMICALS.

Section I.—Preparation of Plain Collodion.
Section II.—Formulæ for solutions for Collodion Positives.
Section III.—Formulæ for solutions for Negatives.

SECTION I.

Preparation of Plain Collodion.

This includes the manufacture of the Pyroxyline and the solution of the same in mixed Ether and Alcohol.

Photographic Pyroxyline may be made either from Linen, Calico, Paper or Cotton-wool. For reasons which are more fully stated in the First Part of the Work (p. 112 *et seq.*), the Writer proposes to confine his observations to the use of the latter material.

The manufacture of Collodion in large quantities, and of a perfectly uniform quality, is a delicate operation, and one which requires great nicety in conducting it. For the amateur who wishes to prepare only as much as will suffice for his immediate wants, it will be better to describe a process more easy of execution, and capable of yielding a moderately good product without liability to failure. The

"Nitre process," as it is termed, is a convenient method of the latter kind, and the process "by mixed acids," which will be found at page 260, will fulfil the requirements of the commercial manufacturer. In either case it will be desirable to consult the Vocabulary, Part III., for the mode of testing the purity of the chemicals.

THE NITRE PROCESS FOR PYROXYLINE.

Use only the best Nitre, as described in the Vocabulary, article "Nitrate of Potash," and having reduced it to powder, dry it on a hot metal plate, or in an oven heated to a temperature above that of boiling water: then pulverize a second time, to prevent the formation of lumps on adding the Oil of Vitriol. Take of

Oil of Vitriol	6 fluid ounces.
Dried Nitre	3½ ounces (avoirdupois).
Water	1 fluid ounce.
Best Cotton Wool . . .	60 grains.

Mix the Acid and Water in a teacup, or any porcelain or stoneware vessel, and throw in the pulverized Nitre by degrees. stirring meanwhile with a glass rod, until lumps disappear, and a transparent viscid liquid is obtained. This will occupy several minutes.

Pull out the Cotton into separate balls of the size of a walnut, and when a mercurial thermometer,* dipped in the acid and stirred backwards and forwards, remains stationary at 145° to 150° Fahr., immerse the balls singly with a glass rod, and press each against the sides of the cup. This part of the operation ought not to take more than two minutes. Supposing the acid to have cooled down below 140° during the pulling out of the Cotton, float the cup upon boiling water for a few minutes until the exact temperature is attained. Leave the Cotton in ten minutes, and afterwards pour off the excess of the acids and squeeze the Pyroxyline with the glass rod. Do this quickly, and then dash the cup and its contents suddenly into cold water, moving the Cotton backwards and forwards with the hand until it feels perfectly cold.

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* In the preparation of soluble cotton, a thermometer is indispensable. Instruments of sufficient delicacy for common purposes are sold in Hatton Garden and elsewhere, at a low price. The bulb should be uncovered, to admit of being dipped in acids, etc., without injury to the scale.

Complete the washing of the Cotton, either by leaving it for three or four hours in a slowly-running stream of water, or by squeezing it with the hand like a sponge, for twenty minutes or half an hour; after which it may be spread out upon a cloth, and allowed to dry spontaneously.

The above description of this process is brief, but more complete details as to the manipulation will be found at page 263. The chances of failure are very slight, if the Sulphuric Acid be sufficiently strong, and the sample of Nitre not too much contaminated with Chloride of Potassium. If however a failure should occur from the Cotton dissolving in the acid, the operation must be repeated with a drachm less Water.

Careful directions for dissolving Pyroxyline in the proportions for plain Collodion, and also for making the iodizing solution, will be found at pages 265 and 284. If however the amateur wishes simply to make a few ounces of ready-iodized Collodion for present experiment, he may save himself the trouble of referring to the pages alluded to by proceeding as follows:—Dissolve 2 grains of Iodide of Potassium or Ammonium, and a corresponding quantity of the Iodide of Cadmium, in 3½ drachms of Alcohol of ·815 to ·825 sp. gr.; next add 5 grains of Pyroxyline, and 4½ fluid drachms of Ether of ·725, at 60° Fahr.; agitate until dissolved, and in twelve hours the upper part may be decanted for use; it will retain a fair portion of sensitiveness for a month in cool weather. For direct Positives on glass add one grain of Bromide of Ammonium to each ounce of the above.

COMMERCIAL MANUFACTURE OF PYROXYLINE BY THE PROCESS WITH MIXED ACIDS.

This process will be described with more minuteness than the last, since it is intended for the use of the manufacturer, who has to satisfy the requirements of the professional artist, and to produce an article as nearly uniform as possible.

The formula for the Nitrosulphuric Acid will vary according as the Pyroxyline is intended for Positive or Negative Collodion, and the proportions of the solvents also will be different in the two cases; the general details of the manufacture however will be the same. The subject may be divided thus:—the Chemicals; the Apparatus; the Preparation of the Collodion; the Precautions to be observed.

The Chemicals.— These include Cotton, Sulphuric Acid, Nitric Acid, Ether, Alcohol, Iodide of Potassium, Iodide of Ammonium, Iodide of Cadmium, and Bromide of Ammonium. To economize space, and to simplify the arrangement of the Work, the Author has placed these chemicals in the Vocabulary, Part III., where they will be found arranged according to the initial letter of the principal constituent.

The Apparatus.—The following articles will be found useful in preparing Collodion on a large scale:—

a. *Porcelain pots for the acid.*—These are about seven inches high, four inches in width at the top, and are provided with covers and handles; also with a rim near the upper part, which serves as a support when heat is applied. The glaze is very good, and is unaffected by the acid. They hold an imperial pint and a half. The form of the vessels is not unimportant, for a wide and shallow vessel exposes so large an evaporating surface, that fumes are given off abundantly, and the strength of the mixture is soon affected. Porcelain pots of the above form may be purchased of Messrs. Brown, medical glass warehouse, Farringdon Street, London, E.C.

b. *Glass spatulas.*—These are made of thick plate-glass, and may be obtained at Messrs. Brown's warehouse, Farringdon Street. Length ten inches, breadth one and three-eighths of an inch, thickness one quarter of an inch.

c. *Hot air Bath.*—This is a simple apparatus for warming the pots containing the acid mixture, when the temperature is inadvertently allowed to fall too low. It consists of an open vessel like a saucepan, made of sheet-iron fastened by rivets, standing on legs over a Bunsen's burner. In the part corresponding to the cover of the saucepan is a round hole, into which the porcelain pot drops, until it is caught and supported by the rim. The pot does not touch the bottom, but approaches very near to it, and hence all danger of cracking is avoided, whilst sufficient heat can be obtained in a few minutes.

d. *Thermometer.*—Select an instrument with a wide column of Mercury, so as to be easily seen by gaslight, and with a large bulb, that it may be sufficiently sensitive. It is quite necessary to compare the thermometer with a standard instrument, since the cheaper thermometers constantly vary, to the extent of several degrees. It is useful also to have a second thermometer with which to compare the first, since the column of Mercury sometimes separates, leaving a vacant space, and thus indicating too high a temperature.

e. *India-rubber gauntlets.*—These are indispensable, as a protection to the hands in making large quantities of Pyroxyline: they may be obtained of Messrs. Matthews and Son, Charing Cross.

f. *Trough for washing.*—It consists of a strong deal framework, three feet long by two feet wide, lined inside with gutta-percha. The water passes in through two tubes, one at the end and the other near the centre, each being pierced with fine holes, so as to deliver the water in a series of jets, and thus to keep up a constant current at every part of the tray.

g. *Steam Bath for drying Cotton, etc.*—This may be made by first constructing a flat zinc tray, two feet wide by four feet long, with a tightly soldered cover, and standing on short legs. The water is boiled in an ordinary tin saucepan, and the steam conducted by a pipe about three feet long, well rolled in list or flannel, into the closed tray, the condensed water being allowed to drop out at the end. Pyroxyline may be dried with safety upon this bath, when the flame is placed at a sufficient distance, since the heat can be regulated at will by adjusting the supply of gas. If the upper zinc plate be covered with flannel or calico, the temperature does not rise higher than 130° Fahr.

THE MANIPULATIONS.

We commence with Pyroxyline for Negative Collodion, and at page 247 will add the few remaining particulars which apply to Positive Collodion.

a. *The Pyroxyline.*—The Writer always adopted the plan of laying in a large stock of acids at one time, since it was somewhat troublesome to ascertain the exact strength, and no mode of analysis seemed perfectly satisfactory. Three carboys of Oil of Vitriol were sent in, holding six gallons each (the strongest obtainable), and one carboy of strong Nitric Acid of the same size. These were bottled off into Winchester quarts, or half-gallon stoppered bottles (labelled No. 1 for the first Carboy, No. 2 for the second, and No. 3 for the third), for the sake of greater convenience in handling, and to lessen the chance of the acid absorbing water from the atmosphere. As the strength of the Oil of Vitriol in each carboy differed, a mixture was made of No. 1, No. 2, and No. 3, taking a single bottle of each. Then, supposing the specific gravity of the acids to be nearly as before given, the formula will stand as follows:—

Oil of Vitriol, 1·845 at 60° Fahr.	18 fluid ounces.
Nitric Acid, 1·457 at 60° Fahr. .	6 fluid ounces.
Water*	5¼ fluid ounces.

Pour in first the water, then the Nitric Acid, and lastly the Oil of Vitriol; obtain a perfect admixture by stirring, and take the temperature. If the thermometer rises to 165° Fahr. or 170°, the acid must be allowed to cool until it stands exactly at 150° Fahr. Then immerse the Cotton in pieces well pulled out, and weighing thirty grains each, continuing to put them in singly until *ten* have been introduced, making 300 grains in all. This operation, together with the pressing against the sides of the vessel, etc., to be alluded to again presently, will occupy about a minute and a half, after which the vessel may be covered up and left for nine minutes. The process is complete in half that time, but the extra five minutes, although producing a little more solution of the Pyroxyline, and consequently diminishing the weight of the product by about 15 per cent., produces a Collodion which is less likely to show glutinous markings upon the glass, or to dry up speedily and repel the developer. Lastly, take out the Pyroxyline in one lump with glass spatulas; squeeze out as much of the acids as possible in a porcelain capsule, and dash the whole into a large quantity of water.

With regard to the temperature at which the Pyroxyline should be made, the Author worked at first at 140° Fahr.; but was eventually induced to raise it ten degrees, in consequence of representations that the Collodion was somewhat deficient in fluidity. This increase of temperature, however, assists in generating traces of a body (probably Nitro-Glucose) which causes the Collodion to lose its sensitiveness more rapidly after iodizing.

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* Most who have tried this formula complain that the Cotton *dissolves*, unless the quantity of water be reduced to five ounces. The Writer however finds that by a careful attention to the purity of the chemicals, he is always able to work with more water than that given, so that he prefers to leave the formula as it stands.

An experienced person will be able to judge on lifting the Cotton out of the acid whether he has hit the right point. If, on attempting to lift out the whole mass of Pyroxyline at once with the glass spatulas, it seems rather small in quantity and very rotten, so that little pieces break away and are left behind in the acid, then the temperature was too high, or the acids too weak, and in repeating the operation the water must be diminished by two or three drachms in the quantity of acid given above. If, on the other hand, the mass of Pyroxyline appears large, sticks well together, and shows no tendency to tear, either the temperature has fallen several degrees, or it will be advantageous to work with a few drachms more of water.

Whilst the Pyroxyline is washing in the tray, it is still more easy to judge of its quality; for if the ten separate pieces, in which the Cotton was originally weighed, are seen floating about, and can be separated and counted, the acids were certainly too strong; whilst if there be an evident aspect of commencing solution—a piece of Cotton here and there scarcely changed, but the others in a measure broken up, and tearing easily under the finger,—the operation is probably successful; but when the whole is so mixed up together that nothing but fragments of the ten pieces can be detected, then the acids were too weak, unless the temperature was inadvertently allowed to fall.

It takes twenty-four hours to ensure the proper washing of the Pyroxyline, even in a slowly-running water which contains a portion of chalk; this Carbonate of Lime evidently acts in neutralizing the acid, and bubbles of Carbonic Acid gas form, which bring the Cotton by degrees to the surface of the water, and keep it floating.

After a thorough washing, the Pyroxyline is squeezed in the hand, and then picked out to dry upon a cloth. A boy performs this part of the operation; and after a little experience, he can tell easily whether the material was properly made, partly by the extent of surface which it covers upon the cloth, but more easily by the readiness with which it tears under the fingers. If it resembles the original Cotton in appearance, and feels strong and tough, the amount of water in the acids must be increased; but when it breaks up into little bits, it is correctly made, or else is somewhat too weak, in which case the fragments will mat together, so as to increase the difficulty of picking them out. As the Pyroxyline dries upon the cloth, it will be well to examine it and give directions accordingly, separating any piece which appears less acted on than the rest; this piece was probably the piece put last into the acid and left at the upper part of the liquid.

Two or three days' exposure to the air will render the soluble Cotton sufficiently dry; but it is convenient to finish it off on the hot steam bath before described, and the temperature in which must not be allowed to rise higher than 120° Fahr. When dry, proceed to weigh it in the scales, and form your estimate of its value accordingly. A long experience tends to show that, supposing nothing to be lost in the washing, the weight of the resulting Pyroxyline is a certain and safe guide in this process, and it is always possible to tell what the quality of the Collodion will be by using the scales. If 300 grains of Cotton yield 450 grains of Pyroxyline, it is certain that complaints will be made of the resulting Collodion being thick, and giving streaky pictures: four or five additional drachms of water in the above quantity of Nitro-Sulphuric Acid will be the remedy. When the weight of the Pyroxyline is the same as that of the original Cotton, viz. 300 grains, there will be a sediment on dissolving it in the mixed Ether and Alcohol; nevertheless the Collodion, although lessened in quantity, will be good,—very limpid and structureless, with great adhesion to the glass, less tendency to markings of all kinds, and considerable softness of Negative, with sensitiveness to dark rays. The chance of spots, however, is peculiarly great with this Collodion; for if the smallest particle of dust touch the film, it will almost certainly arrest the development, and produce a transparent circular mark (p. 48).

The weight which on the whole appears to be best is 375 grains, that is to say, exactly 25 per cent. of increase: this gives sufficient fluidity of Collodion, and at the same time leaves very little sediment in dissolving.

The above facts are quite reliable, since they have been verified by repeated observation, extending over a long time. It must, however, be distinctly understood that the weight of the Pyroxyline can be taken as a criterion of quality only under the conditions stated,—the fibre of the Cotton must be cleaned by Potash *and quite dry*, the Nitric Acid nearly free from Chlorine, the time of immersion always the same, and, most important of all, the temperature correctly ascertained, otherwise the weight will be so variable that nothing can be deduced from it, and the Cotton will be considerably acted on, even when the acids are strong enough to produce an explosive variety of Pyroxyline. The whole process, in fact, requires care, because it is conducted with the maximum quantity of water, and at a high temperature. At least twenty per cent. of the Pyroxyline is dissolved in any case; and the acids having once begun to act, will readily destroy the remaining portion of the fibre, if an error be permitted.

Before passing on to the preparation of the Collodion, it may be mentioned that the quantity of Pyroxyline which it is convenient to make at one operation is four times that stated. A double quantity of acids is mixed in a jug (thirty-six ounces of Sulphuric and twelve of Nitric), and poured out into the porcelain pots before mentioned. The first three hundred grains of Cotton are then immersed, and left digesting whilst the second similar portion of Cotton is put into vessel No. 2. When the Pyroxyline has been removed, the acids are emptied out, and a double quantity again mixed as before. At one time the plan was adopted of using the old acids again, by adding Oil of Vitriol to restore the strength, but afterwards it was discontinued as causing uncertainty.

b. *The Plain Collodion.*—This is made by introducing half a gallon of Alcohol of ·805 into a two-gallon stoppered bottle, and adding 1900 grains of dry Pyroxyline. When the soluble Cotton has become thoroughly saturated with the Alcohol, pour in half a gallon of Ether of ·725, and agitate for two or three minutes; next add another half-gallon of Ether, and again shake the bottle for a few minutes. After this the Collodion may be allowed to settle for about a week or ten days, when it will be sufficiently clear for use: no plans for filtering have been found to answer. The quantity of Pyroxline may be increased to 2200 grains when a Collodion of some body is required, or reduced to 1800 for a thin Collodion suitable for large plates. Something, however, in this respect depends upon the proportion of undissolved sediment, which is always greater when the acids are used with the full quantity of water. Supposing the height of the column of Collodion as it stands in the bottle to be ten inches, the sediment when measured twenty-four hours after mixing is often about half an inch, but it settles down more closely at the expiration of a week or ten days. If the sediment should stand as high as two inches in the bottle, the Collodion is probably of that kind which has been described as giving a soft Negative with a tendency to white spots. The above point being of importance in a commercial point of view, pains were taken to collect the sediment from more than two hundred gallons of Collodion, and it was found that the loss did not exceed one pint in fifty. It appeared at first to be much greater than this, but the residue continued to settle for many months, the clear Collodion being occasionally drawn off from the upper part and mixed in with the general stock, a little at a time.

The proportions of Ether and Alcohol in the above Collodion will be found to be those best adapted for general purposes. With less Alcohol the film is more contractile, and more prone to dry up after sensitizing. With a larger proportion of Alcohol, say five parts of Alcohol of ·805 at 60° to three of Ether of ·725 (these proportions are for the *Iodized* and not the Plain Collodion) the sensitiveness is impaired; as also is the adhesion to the glass. The Alcoholic formula is well adapted for coating large plates, and is sufficiently sensitive for copying works of art or landscapes: nevertheless it is not recommended in preference to the other for a normal Collodion, seeing that we have no means of increasing sensitiveness when it proves deficient.

On the day following the preparation of the Collodion, about half of a fluid ounce may be drawn off by a pipette from the upper clear portion, and a small piece of red and blue test-paper immersed for twelve hours. If, at the expiration of that time, the blue paper appears reddened, the Pyroxyline was imperfectly washed, and the standard alkaline solution, which will be immediately described, is dropped into the plain Collodion in the proportion of one full-sized drop to each half-gallon. This addition of Alkali was seldom required in the Writer's practice; certainly not oftener than once in twenty times. When, however, the Pyroxyline was removed from the washing-tray at the expiration of twenty-four instead of forty-eight hours, traces of acid could generally be detected in the Collodion. To make the standard solutions which are required, dilute the Nitric Acid of 1·45 with an equal bulk of water for the acid, and then dilute down the strong Ammonia of commerce also with distilled water, until a fluid drachm exactly neutralizes a corresponding bulk of the standard acid. With these two liquids at hand no further trouble will be experienced, since the quantity of acid left in the Pyroxyline varies very little; and if any number of drops of Ammonia be added in excess, a corresponding number of the acid liquid will neutralize them.

PRECAUTIONS TO BE OBSERVED.

Attention may be directed to certain minor details of manipulation, which are in themselves simple, but may be unknown to some who desire to carry out the instructions contained in this paper.

Beginning with the Cotton, it will be necessary to cleanse it by boiling with Potash as described in the Vocabulary, Part III.; and if this process of cleansing be properly performed, a second boiling with fresh Potash ought not to produce any yellow discoloration of the liquid. The washed Cotton must be dried by artificial heat, and if not to be used immediately, may afterwards be put away in a drying-box, which can be economically constructed by making a false bottom to an ordinary trunk, piercing it with holes, and placing beneath it a shallow dish containing Oil of Vitriol: it will then be sufficient to lift the cover and throw in the balls of dried Cotton to ensure their remaining perfectly dry; whereas on the other hand, if the Cotton be left in a damp place, it will absorb water from the atmosphere.

In mixing the acids, it simplifies matters to begin by selecting a stoppered bottle which holds the proper quantity of Oil of Vitriol when filled quite up to the neck. The Nitric Acid and the water may be measured in a narrow cylindrical hydrometer glass; a mark being made for the former with black varnish, at a height corresponding to one-third of the bulk of the Oil of Vitriol, and a second mark lower down for the water, the quantity of which will vary according to the strength of the acids. Before using these measures, always invert them, and allow the drainings from the last operation, consisting of acid diluted by absorption of atmospheric moisture, to flow out. Then measure the Oil of Vitriol, and make a leaden counterpoise for it in the scales, bottle included. This is necessary when perfect accuracy is desired, since otherwise the Nitro-Sulphuric Acid will be stronger in winter than in summer, which the Writer always found to be the case to a noticeable extent; the product of Pyroxyline obtained from three hundred grains of Cotton being fifty grains heavier in frosty weather than during the hot months of June and July. It is not absolutely necessary to weigh either the Nitric Acid or the water; and, with regard to the Sulphuric Acid, the plan usually adopted was to measure it as a rule, but to put the bottle afterwards into the scales, if a sudden change of atmospheric temperature took place.

A failure would certainly be produced if the three constituents of the Nitro-Sulphuric Acid were not properly mixed; but there is no difficulty in effecting this by stirring with the broad spatula for half a minute in a shallow vessel. In the deep porcelain pots before spoken of, it may not be quite so easy, and hence it is advantageous to adopt the plan of mixing a double quantity of acids in a jug, and pouring it afterwards into the pots. The sides of the jug, however, must not be too thick, or the temperature will sink below 150° in very cold weather, especially when the Sulphuric Acid is a little weaker than usual, or the mixture is kept too long in the jug.

Some may perhaps be inclined to keep a portion of the Nitro-Sulphuric Acid ready prepared, and to obtain the correct temperature by mixing cold acid with the hot. If so, bear in mind that a stoppered bottle must be used, since Nitro-Sulphuric Acid, like Oil of Vitriol, absorbs water from the atmosphere. On one occasion some experimental results were completely spoilt, by leaving the acid for a few days in a beaker covered by a glass plate; the upper part became so far weakened that, on putting in the Cotton, it instantly dissolved.

Taking the temperature of the acids is an operation of some nicety, and especially so in cold weather. Begin by stirring briskly with the glass spatula in a circular direction; then dip the thermometer exactly into the centre of the liquid, and hold it in that position for at least a minute, since the rise of the mercury, although rapid at first, is very slow towards the end. If the acid is too hot, it can be cooled two degrees by taking a cold spatula and stirring it for a few seconds; therefore it is of consequence that the spatula which is used to immerse the cotton should be previously warmed by dipping it in the liquid. The acids also must be at least at 165° Fahr. when they are first placed in the porcelain vessel, otherwise its thick sides will reduce the temperature so rapidly that, although the thermometer may indicate 150° Fahr. at first, it will soon fall, and the weight of the resulting Pyroxyline will be greater than that indicated for a given strength of acids. In order to obtain a uniform temperature during the time that the Pyroxyline remains immersed, large jars may be inverted upon the porcelain pots, so as to prevent them from being cooled by contact with the external air.

The boy who weighs the Cotton into pieces of 30 grains each, should be directed to pull out each piece thoroughly, and to work it with his fingers into a circular form, so as to facilitate absorption of the acid. In pursuance of the same object, each piece, as it is placed in the acid, is carefully pressed with the spatula against the side of the vessel; and in order that the last pieces may not be at the top (in which case they always come out less broken than the others), a *well* of acid is kept free by means of the spatula, and these last pieces are pushed down nearly to the bottom. When all have been immersed, the mass is squeezed against the vessel, first on one side and then on the other, after which the whole is loosened by putting the spatula down to the bottom, and raising it up until the Pyroxyline nearly fills the liquid; the vessel is then covered up and left for nine minutes, as before said. It is better not to finish the process of putting in the Cotton by pressing it down to the bottom in a hard mass, because a good deal of solution always takes place in the acids, and this is attended with an evolution of *heat*, which increases the disintegrating action on the Cotton. The object, therefore, is to prevent the mass from "heating," as far as possible, by loosening it out with the spatula and diffusing it through the liquid. Observe, however, that the Cotton must not be permitted to project above the surface into the air, or oxidation and evolution of red fumes will take place.

Both spatulas are employed in removing the Pyroxyline from the acids, by forcing them down to the bottom on opposite sides, and then bringing them together so as to pinch the mass and lift it out entire. In squeezing the acids away, no time must be lost, or the action of the air will produce oxidation and red fumes. A few seconds will be sufficient, and especially so if great pains be taken to distribute the Pyroxyline through the water by catching it with the gloved hand. A sensation of heat is felt at first, due to dilution of the Oil of Vitriol; but this soon ceases, and the chance of failure from that cause is very slight. If the material, however, were simply thrown into a small quantity of water and allowed to remain, the rise of temperature might be sufficient to cause solution.

It was conjectured at first that the waste Nitro-Sulphuric Acid —which if thrown down the sink would be likely to act upon the leaden pipes—might be useful for some other process. This expectation, however, proved fallacious, since the Pyroxyline which it contains in solution appears to interfere with its application to any such purpose as dissolving metals, etc.

At first it was thought sufficient to place the Pyroxyline in the gutta-percha washing-dish immediately on taking it from the acids; but finding that the heat and acid together gradually decomposed the gutta-percha and made it sticky, the plan was afterwards adopted of throwing the soluble Cotton first into a a leaden sink, and when the greater part of the acid had been removed by a few hours' washing, lifting it out into the gutta-percha dish.

The gutta-percha washing-tray will require cleansing after a week or so; a deposit adheres to the bottom, which seems to consist of matted fibres of partially dissolved Pyroxyline. This material having been some time in the water, would be likely to decompose and liberate Oxides of Nitrogen in the Collodion. It is better therefore not to disturb it at first; and when sufficient has collected, it may be scraped out, and the tray washed with water.

It is advisable not to complete the washing of the Pyroxyline with boiling water, nor to use any carbonated or caustic alkali to remove the last traces of acid. All alkalies tend to decompose Pyroxyline, and remove a portion of the Peroxide of Nitrogen in the form of Nitrite; and although dilute Ammonia is commonly employed to neutralize the acid, it will be found that some varieties of Pyroxyline assume a yellow colour, and become more unstable in Collodion when previously treated with Ammonia.

The Pyroxyline may be prepared in small quantities at a time, as required for use; but if it be necessary to keep it in stock, it should be dried either over Oil of Vitriol, or at a temperature below 120° Fahr. Mr. Hadow mentions 140° Fahr. as the point which ought not to be exceeded. Probably something depends upon the particular variety of Pyroxyline; but with some kinds red fumes will be given off, on placing the material in a covered tin vessel surrounded by boiling water. Pyroxyline for keeping ought also to be put away in a dry place, and excluded from light, since this substance is known to be liable to spontaneous change, and unfortunately the exact conditions of permanency have not been ascertained.

Having completed the preparation of the Pyroxyline, this list of "Precautions" is nearly at an end: a few words on the subject of plain Collodion will close it. For holding the Collodion narrow-mouthed stoppered bottles may be used, containing two gallons each: they may be obtained of Messrs. Brown and Co., of Farringdon Street.

There is a decided advantage in placing the Alcohol in the bottle before the Ether, not only in facilitating the solution of the Pyroxyline, but also in enabling the operator, by shaking the bottle, to remove a flocculent deposit, which otherwise is apt to adhere, and to be drawn over with the Collodion; the mass of Pyroxyline wetted by the spirit acts effectually as a *mop*, and cleanses the sides.

In drawing off the Collodion, place the bottle in such a position that the end of the siphon comes between the eye and a strong light; any flocculi which appear likely to be drawn into the end of the siphon will then be seen, and may be avoided. When it is not intended to refill the bottle immediately, pour out the sediment and introduce half a gallon of absolute Alcohol, which will absorb the remaining Ether vapour, and prevent it from being oxidized into Acetic Acid, and afterwards forming Acetic Ether. On one occasion a two-gallon bottle having been used for Collodion and left empty, was put away in a dark place for about three months. It was then washed out with about a pint of plain Collodion and refilled. The result, however, was unsatisfactory; for on adding the iodizer to the newly made batch, it at once became yellow, which was probably due to portions of Collodion left at the bottom of the bottle having decomposed and ozonized the Ether. Mere washing with plain Collodion was not sufficient in this case, and a thorough cleansing with shot and water should have been resorted to.

No attempt must be made to utilize the sediment of the plain Collodion by re-distilling the Ether from it. This has been tried, but with indifferent success; for although the Ether so recovered appeared tolerably good at first, it soon acquired the property of liberating Iodine from Iodide of Potassium, and the Collodion then became unfit for any purpose excepting copying objects of still life, where extreme sensitiveness is not required.

Whilst the Collodion is settling down, the bottle should be covered over, to exclude the light. The room which the Author used was a vault lighted by gas; and whilst plain Collodion remained in that room, it continued good; but if any portions were taken up into the glass-house and left exposed, they gradually deteriorated, colouring at once on adding the Potassium iodizer, and losing sensitiveness.

In manufacturing Collodion in large quantities, mistakes will be prevented if separate measures, scales, funnels, etc., are kept for each purpose; and in cases where two operations are being carried on at the same time—such as picking out wet Pyroxyline, and filtering iodizing solution—a basin of water may be placed near at hand, into which the boy dips his fingers in passing from one process to the other. The mention of matters so trivial may appear unnecessary; but the importance of extreme method in all matters relating to Photography is sometimes overlooked.

Minor precautions to prevent accidents.—Several cases of accident in making Collodion having come to the Writer's knowledge, he feels it a duty to give plain instructions to those who are not practical chemists.

Beginning with the preparation of the Pyroxyline, it may be observed that the vessel containing the acids must be placed either in the open air, or beneath a flue, to carry off the fumes; and as Nitro-Sulphuric Acid, especially when heated, is a most corrosive substance, the hands of the operator should be protected by the gloves of vulcanized india-rubber before described; otherwise, after repeating the process a few times, the skin and nails will become rough and yellow from the action of the fumes. Of the two acids the Nitric Acid is the most destructive, and it sometimes happens that a minute drop spurts into the face. To avoid this, be careful when pouring acids *from a full bottle* to hold the neck very near to the recipient vessel, and to allow the acid to flow gently against the sides without any gurgling; and when removing the stopper, throw an old cloth over the bottle, to prevent a sudden rush of vapour from projecting the acid. Have at hand a small quantity of tow to wipe up any acid which may run over the sides, and if the fingers are touched, wash them immediately in water, before they become yellow.

A drop of either acid may fall upon the clothes; if *Sulphuric*, a red spot is at once produced on black cloth or leather, but it disappears on treating with strong Ammonia and subsequent washing; Nitric Acid or Nitro-Sulphuric Acid, however, will almost certainly make the cloth rotten and yellow, unless the Ammonia be applied instantly.

In mixing the acids, avoid by all means the use of any kind of vessel which is likely to crack under a sudden rise of temperature, and in particular of a *stoppered* vessel, on account of the disengagement of vapour which takes place. In one instance where this precaution was neglected, a stoppered Winchester quart, containing thirty ounces, was instantly blown to pieces.

In disposing of the waste acids, it is necessary to dilute very freely with water before throwing them down the sink, or the leaden pipes will soon be destroyed. If they are stowed away for a time in bottles, see that the bottles have not previously been used for Ether or Alcohol, since warm Nitro-Sulphuric Acid inadvertently poured into a bottle with a little Ether at the bottom, produces a violent effervescence of red fumes. For this reason also, the same glass measure ought not to be employed both for Collodion and acids, unless carefully cleansed; for organic matters of a kind so easily susceptible of oxidation, will invariably produce decomposition and spirting with hot Nitric Acid.

Fears are sometimes entertained of the Pyroxyline itself exploding during the process of manufacture; but these are groundless. It may, indeed, decompose rather suddenly and evolve red fumes, as before shown, but in that case the action would be stopped by throwing it into a pan of water. The use of artificial heat in drying Pyroxyline, however, has been the cause of very severe explosions, when, from evaporation of the water in the boiler or from other causes, the heat has been allowed to rise.

Accidents result sometimes from carelessly handling Ether, and especially from attempting to conduct the distillation of Ether without the proper apparatus. Those who have seen an Ether distillery, know that extraordinary precautions are always taken to prevent the vapour from flowing along the ground and reaching the source of heat: and when we consider the very low temperature at which Ether boils, and the chance of the retort bursting from sudden evolutions of vapour, it is evident that the process ought not to be attempted, excepting by a practised chemist.

When Ether is kept in bottles only partially full, the stopper will sometimes blow out suddenly in hot weather, and may fall upon another bottle near at hand. Avoid this, by purposely fixing each stopper with a twist, or passing over it a slip of vulcanized rubber. In shaking a bottle containing Collodion, examine it first for *cracks*, and if it is only partially full, fix the stopper with the finger, and also loosen it between each shake, so as to permit of the escape of the pent-up vapour.

Collodion ought not to be prepared in large vessels like carboys, which are often made of badly annealed glass. A carboy of Collodion, containing about three gallons, has been known to burst suddenly, when the temperature of the atmosphere has risen to the summer heat.

In entering a dark room or a cellar containing much Collodion, if a candle be absolutely required, *hold it high above the head*, inasmuch as the vapour of Ether is very dense, and soon falls to the ground. Amateurs sometimes meet with mishaps in coating glasses with Collodion, from forgetting this fact, and placing a naked candle *below* the level of the plate.

If a beaker or any other vessel containing Ether or Alcohol should catch fire, do not attempt to extinguish it with water, but throw a thick cloth over the mouth of the vessel, so as to cut off the supply of air.

PREPARATION OF POSITIVE COLLODION.

The plain Collodion described in the preceding pages may be used for Positive as well as Negative pictures, if the iodizer be made with mixed Iodide and Bromide (see p. 284); but it has been deemed advisable to give a formula for a Pyroxyline producing a less vigorous image than that prepared in the Nitro-Sulphuric Acid containing an excess of the diluted Sulphuric Acid.—Take of

Oil of Vitriol 1·845 at 60° Fahr. . . .	12 fluid ounces.
Nitric Acid 1·45 at 60° Fahr. . . .	12 " "
Water	3¼ " "

Mix these ingredients, and allow the temperature to fall to 140°

Fahr. The Cotton may be the same as before, and the Writer adopts the plan of cleansing it with Potash precisely as described in the Vocabulary: also of drying it artificially before immersion. Supposing these precautions to be neglected, it is more than probable that it will be necessary to reduce the quantity of Water in the formula from 3½ down to 3 ounces, as the Nitro-Sulphuric Acid is undoubtedly very weak, and would not bear any further dilution.

The Cotton when immersed in the above mixture behaves differently from that dipped in the Nitro-Sulphuric Acid containing the excess of diluted Sulphuric Acid, and the appearances described at page 263 as indicating the strength of the acid cannot in this case be relied on. When the acid of the formula now given is too weak, the Cotton sinks down almost to the bottom, occupying but little space, and matting together until it forms a mass like "felt;" it also becomes very opaque, and gelatinizes in the acid. On lifting it out into the water it sticks together so that the fibres cannot be separated from each other, and the action of the water in washing out the acid is interfered with. Supposing the acids, on the other hand, to be too concentrated, the Cotton is little altered in appearance, and is very strong and tough, so that it may be well handled without tearing. These appearances are described from experiments in which the Cotton had been both boiled with Potash and dried; they may not accord exactly with the experience of those who use ordinary Cotton, the effect of which would be to favour disintegration and solution in the Nitro-Sulphuric Acid.

The Author's experience in Positive Collodion is not so great as in Negative Collodion, and hence he deems it advisable to acquaint the reader with the opinions of those who have differed from him in their formulæ. The following extract is from a paper read at the North London Photographic Association by Mr. G. Wharton Simpson:—"The formula I have found to give uniform success, both in my own hands and that of others, is one an approximation to which is, I believe, commonly used, but which I find given definitely by Mr. Sutton: it is as follows:—Of Sulphuric Acid sp. gr. 1·840—the Oil of Vitriol of commerce is sufficiently near the mark—and of Nitric Acid sp. gr. 1·420, equal parts by measure. To three measured ounces of the mixed acids, one drachm of Cotton-wool will be about the right quantity. The time of immersion not less than five minutes, the temperature being maintained at about 150°. I have found that the Nitric Acid most commonly sold, commercially, as pure Nitric Acid, has generally a sp. gr. of 1·360; and in this case I have found that six measured parts of Sulphuric Acid to four of Nitric Acid of this strength give an excellent soluble Cotton. In either case the Cotton gains fully fifty per cent. in weight, and yields an even sensitive film, adhering well to the glass, and quite transparent in the shadows.

"Six grains of either of these Cottons will dissolve perfectly, with scarcely a perceptible residue, in equal parts of washed Ether, sp. gr. ·750, and Alcohol, sp. gr. ·820. More Cotton would dissolve, but this is sufficient. Alcohol and Ether of these strengths are easily procurable; and I have found after long use that the Alcohol may be used, safely and with advantage, in at least equal proportions with the Ether."

Observe that the acids which Mr. Simpson uses are stronger than those before mentioned, but that the temperature is higher. This would produce a more vigorous picture, and one less likely to exhibit fogging on the shadows. It is not easy to legislate for another in the matter of Collodion, since the length of keeping after iodizing and the purity of the solvents affect the clearness of the developed picture, as also does the state of the Nitrate Bath. With reference to the formula for Positive Pyroxyline given by the Writer, it may be said that its errors are in the opposite direction to those of the formula previously given for Negative Pyroxyline: hence if the former sets too slowly upon the glass, and does not give clean shadows, it may be mixed with the latter, which sets with greater rapidity.

The plain Collodion.—This may be made with the best Methylated Ether, or by preference with the pure Ether of ·728. The Alcohol should be that of ·805 at 60° Fahr.,—sold as absolute:—if absolute Alcohol cannot be obtained, a spirit of ·815 rectified from Carbonate of Potash, or even of ·825, may be substituted: in the latter case the relative quantity of Ether must be increased from 4½ to 5 ounces, and that of the spirit diminished from 1½ to 1 ounce. Take of

Ether of ·725	4½ fluid ounces.
Alcohol of ·805	1½ fluid ounce.
Pyroxyline	48 grains.

Shake up the Pyroxyline first with the Alcohol, and afterwards add the Ether: a little more agitation may be required than in the case of the Negative Collodion, as this Pyroxyline is more apt to form gummy masses at the bottom of the bottle. The Collodion ought to be clearer and more translucent than the Negative Collodion, and to settle in less than one-half of the time; if a thick deposit forms, the acids contained too much water, and the Collodion will probably yield a cloudy film on drying.

The iodizing compound for the Collodion will be found in the formulæ for Positives in the next Section.

SECTION II.

Formulæ for Collodion Positives.

The solutions are taken in the following order:—The Collodion.—The Nitrate Bath.—Developing Fluids.—Fixing Liquid.—Varnishes.

THE IODIZED COLLODION.

The plain Collodion having been made according to the directions given in the last Section, it remains only to prepare the iodizing solution. For this purpose take of

Iodide of Ammonium	1½ drachm.
Iodide of Cadmium	1½ drachm.
Bromide of Ammonium . . .	40 grains.
Alcohol ·805 to ·816	10 fluid ounces.

Read the Vocabulary for the mode of testing the purity of these compounds. The Iodide of Ammonium especially, is liable to vary in quality.

Reduce the salts to powder, and shake them in a bottle with the Alcohol: no heat will be required.

This iodizer becomes yellow on keeping, from liberation of Iodine, but not to an extent calculated to do injury. It must not be exposed to the light, and should be kept in a cool place.

The plain Collodion ought to be kept in the dark, or the Ether will rapidly be ozonized by the Pyroxyline (p. 104). A cool cellar or cupboard will answer the purpose.

The proportions for mixing are *three parts* of Collodion to *one* of iodizer; that is to say, six fluid drachms of the former, to two fluid drachms of the latter.

The film produced by the Collodion, on dipping in the Bath, ought to be tolerably dense and creamy, and if it be opaline or pale-blue, the plain Collodion is too thin. In that case add more Pyroxyline, which in most cases will be sufficient to increase the opacity to the desired extent. Bear in mind however that the presence of Bromide always tends to make the film appear rather less opaque, and therefore it will be better to try a picture before condemning the Collodion.

The newly iodized Collodion is exquisitely sensitive, but sometimes fails in giving a vigorous picture with clear shadows. In that case dissolve five grains of Iodine in an ounce of Spirits of Wine, and add a few drops until the fluid assumes a golden-yellow colour.

The Collodion may be expected to produce good Positives for six weeks or two months after iodizing, in cool weather. The exposure is longer than at first, but the pictures are more free from blemish. Positive Collodion, containing Bromide, and developed with Sulphate of Iron, always suffers less from keeping than Negative Collodion: and hence it may safely be put away in stock, ready iodized.

A mixture of the best Ether with absolute Alcohol, 5 drachms of the former to 3 drachms of the latter, is proper for diluting this Collodion, as it becomes thick at the bottom of the bottle.

In order to convert old brown residues of Negative Collodion into Collodion for Positives, proceed as follows:—Weigh out a grain of Bromide of Ammonium for each ounce of Collodion, rub it up in a mortar with the smallest possible quantity of spirit until dissolved, and add it. A turbidity and precipitation of Bromide of Potassium will take place (unless the Collodion contain an unusually large quantity of water), but in twenty-four hours the liquid will clear itself, and may be poured off for use. An additional quantity of *Iodide* will also be required, if the old brown Collodion gives a blue film, as is frequently the case: one grain of Iodide of Cadmium may be added to each ounce.

THE NITRATE BATH.

Re-crystallized Nitrate of Silver. .	30 grains.
Nitric Acid	$\frac{1}{5}$ minim.
Alcohol	15 minims.
Distilled Water	1 fluid ounce.

In the Vocabulary, Part III., directions are given for the purification of Nitrate of Silver for the Bath; also for the testing of distilled water, and the best substitutes when it cannot be obtained.

The Bath must be saturated with Iodide of Silver, and Nitric Acid neutralized if it be present. Weigh out the total quantity of crystals of Nitrate required for the Bath, and dissolve in about twice their weight of water. Then take a quarter of a grain of Iodide of Potassium to each 100 grains of Nitrate, dissolve in half a drachm of water, and add to the strong solution; a yellow deposit of Iodide of Silver first forms, but on stirring is completely redissolved. When the liquid is clear, test for free Nitric Acid by dropping a piece of blue litmus-paper into the strong solution. If at the expiration of two minutes the paper appears *reddened,* Nitric Acid is present, to neutralize which, add a few drops of solution of Carbonate of Soda (ten grains to the ounce of water), until a distinct white turbidity, remaining after agitation, is produced. Then dilute down the concentrated solution with the remaining portion of the water, stirring all the time, and filter out the milky deposit. If the liquid does not at first run clear, it will probably do so on passing it again through the same filter.

Lastly, add the Nitric Acid *to the clear filtered liquid,* and also the Alcohol.

It may appear unnecessary to commence by neutralizing Nitric Acid in a Bath, when the formula directs that the same acid should afterwards be added: but inasmuch as the amount of free acid in commercial Nitrate of Silver varies considerably, a normal solution could not otherwise be obtained. Some employ *Ammonia* for neutralizing the Nitric Acid, but *Nitrate of Ammonia* is then formed in the Bath; and this substance being a solvent of Oxide of Silver, excess of Ammonia renders the Bath very alkaline, even after filtering.

Bear in mind that all the common metals decompose Nitrate of Silver, and consequently, that the Bath must be kept in glass or porcelain, out of contact with iron, brass, etc.

The object of the *Alcohol* in the formula is to make the film amalgamate with the Bath more readily, and thus to hasten the process of sensitizing.

As the bulk of the Bath becomes lessened by use, fill up with a solution containing 35 grains of plain Nitrate of Silver to the ounce, without any Iodide or Alcohol; this will be found sufficient to maintain the strength nearly at the original point.

When the Bath becomes very old and saturated with Ether, it may yield Positives which are streaked and slightly foggy; if so, it will be advisable to precipitate it with a Chloride and prepare a new one.

THE DEVELOPING FLUIDS.

Two formulæ are recommended: the first being the most simple in its preparation, and easy to manipulate with; the second producing a more metallic picture nearly resembling a Daguerreotype.

FORMULA No. 1.

Pure Sulphate of Iron . . .	12 grains.
Glacial Acetic Acid	$\frac{1}{2}$ fluid drachm.
Water	1 ounce.

Consult the Vocabulary for purity of Chemicals, and best substitutes for distilled water. No filtering needed, as a rule.

An addition of Nitric Acid, half a minim to the ounce, makes the image whiter and more metallic; but if too much be used, the development proceeds irregularly, and spangles of Silver are formed.

The Acetic Acid renders the development uniform, by causing the solution of Protosulphate to combine more readily with the film; it has also an effect in whitening the image and increasing its brightness.

This solution of Sulphate of Iron becomes red on keeping, from a gradual formation of *per*salt. When it is too weak, add more of the Protosulphate, but the experience of the Writer is in favour of working with the newly-mixed liquid, since Acetate of Iron and Acetic Ether appear to be formed by decomposition.

Some operators add pure Nitrate of Potash to this developing solution, to form a *small portion* of Protonitrate of Iron. It is said to improve the colour slightly. The proportions are 10 grains of Nitrate of Potash to about 14 or 15 grains of Protosulphate of Iron.

FORMULA No. 2.

This is a mixture of Sulphate and Nitrate of Iron, employed with much success by Mr. Keith of Liverpool, and other operators. Take of

Sulphate of Iron	1½ ounce.
Nitrate of Baryta	1 ounce.
Alcohol	1 ounce.
Pure Nitric Acid	40 minims.
Water	16 ounces.

Reduce the Nitrate of Baryta to fine powder, in a mortar, and dissolve it in the water by the aid of heat. This may be done in a porcelain capsule standing on a tripod, with a spirit-lamp below, or the water may be boiled in a kettle and poured upon the pulverized salt with constant stirring. Next, reduce the Sulphate of Iron also to powder, and when the whole of the Nitrate of Baryta has dissolved, stir the Sulphate into the warm liquid, and continue to stir for three minutes, to ensure a perfect decomposition. A dense white deposit of Sulphate of Baryta forms, rendering the whole milky, but on leaving the capsule for ten minutes, the heavy powder settles to the bottom, leaving a clear liquid of an apple-green colour, with occasionally a little reddening at the edges, from oxidation and conversion into *Per*nitrate of Iron. Throw the whole on a paper filter, and if the liquid at first runs muddy, pass it through the same filter a second time. Drain away as much as possible, and when it has become quite cold, drop in first the Nitric Acid, and then the Alcohol.

The above operation is very simple, but the amateur must be guarded against two or three causes of failure. The Nitric Acid will sometimes oxidize the Iron, and make it red, and it may also act upon the Alcohol. Do not therefore mix the Nitric Acid with the Alcohol, but add them separately, and drop the required quantity of Nitric Acid first into a few drachms of water, to dilute it down and prevent any chance of oxidation. Lastly, fill up with distilled water to the proper bulk.

The solution so formed will contain in each ounce *about* 30 grains of Nitrate of Iron, and 10 grains of Sulphate of Iron; but the Nitrate is so feeble a developer, that 5 or 10 grains additional of the Sulphate may be needed to prevent the formation of spangles on the shadows, when the weather is cold or the Bath very acid.

This developer will keep for two months in cold weather, and probably longer, if the bottles are filled to the neck; hence a stock can be prepared beforehand. It becomes weakened by a partial decomposition, but produces sufficiently white pictures, if a little Sulphate be added. Acetic Acid is purposely omitted from this formula.

THE FIXING SOLUTION.

Cyanide of Potassium	10 grains.
Nitrate of Silver	1 grain.
Common Water	1 ounce.

The percentage of *Carbonate of Potash* in commercial

Cyanide of Potassium is so variable that no exact directions can be given for the formula. It is best, however, to use it rather dilute—of such a strength that the plate is cleared gradually in from half a minute to a minute. The use of the Nitrate of Silver is explained at page 150.

Solution of Cyanide of Potassium decomposes slowly on keeping, but it will usually retain its solvent power for several weeks. In order to escape inconvenience from the pungent odour evolved by this salt, many employ a vertical Bath to hold the solution; but in that case the plates must be carefully washed before fixing, as the Iron salts decompose the Cyanide and produce a blue deposit.

VARNISHES.

Two kinds of varnish are usually employed for glass Positives, the clear varnish for protecting the film, and the black varnish for backing up.

The objection to the use of black japan is its liability to crack, in consequence of which the film splits away from the glass after keeping the picture a few months. To prevent this cracking and to impart elasticity, it is advised to add a portion of Caoutchouc to the solvent. Take of

Caoutchouc	½ drachm.
Asphaltum	4 ounces.
Mineral Naphtha	10 ounces.

Dissolve the Caoutchouc first, and the Asphaltum subsequently; apply heat if necessary.

For the clear Varnish, take

Soft Copal	40 grains.
Benzole	1 fluid ounce.

The solution filters easily through paper, and forms a colourless Varnish which is brilliant and dries without heat.

The Writer cannot speak from experience of the merits of the above receipts. The composition of the best commercial Varnishes is secret.

SECTION III.

Formulæ for Negative Solutions.

THE IODIZED COLLODION.

The plain Collodion having been made according to directions given in the first Section (p. 265), it remains only to prepare the iodizer.

FORMULA No. 1. (Potassium Iodizer.)

Iodide of Potassium	135 grains.
Alcohol of ·816	10 ounces.

FORMULA No. 2. (Cadmium Iodizer.)

Iodide of Cadmium	170 grains.
Alcohol of ·816	10 ounces.

Dissolve in the cold and filter; no pulverizing required.

FORMULA No. 3. (Bromo-Iodizer.)

Bromide of Ammonium	40 grains.
Iodide of Ammonium	90 grains.
Iodide of Cadmium	90 grains.
Alcohol of ·816	10 ounces.

Pulverize and dissolve without heat: filter.

Consult the Vocabulary on the purity of the Iodides, and the varying strength of commercial Alcohol. The proportion in which these iodizing solutions are to be added to the plain Collodion is the same for all, viz. two fluid drachms of iodizer to six fluid drachms of plain Collodion. No. 1 may be mixed with No. 2 in equal bulks when greater stability is desired. No. 3 may also be mixed in any proportion with No. 2: not however with No. 1 in quantity greater than one-third or one-fourth of the bromo-iodizer, otherwise crystals of Bromide of Potassium will be thrown down on iodizing the Collodion. By substituting pure Iodide of Sodium (p. 125) for Iodide of Potassium in No. 1, a larger quantity of Bromide might be introduced without causing precipitation.

Remarks on Formula 1.—This iodizer is the one which the majority prefer: many however mix it with Formula

No. 2, half-and-half. Reduce the Iodide of Potassium to *an impalpable* powder, and shake in a bottle. Perfect solution will scarcely be obtained unless the Alcohol be previously warmed to about 140° Fahrenheit, or the bottle dipped in hot water. The latter plan is simple, but there is a chance of cracking the glass.

The quantity of Iodide of Potassium given is the maximum which the Collodion will carry without producing marks like watered silk at the lower edge of the film.

The film produced in the Bath ought to be tolerably dense, and if it comes out very pale and blue, the plain Collodion may be too thin, and if so, must be thickened by addition of Pyroxyline. Supposing the plain Collodion to be sufficiently thick, and the film too opaline, add to each ounce a single grain of Iodide of Cadmium.

This iodizer usually remains colourless if kept in a dark place, but on exposure to light a trace of Iodine is liberated, tinging it yellow. Re-absorption of the Iodine will occasionally take place on again removing the iodizer from the light.

The plain Collodion must also be kept in the dark, or the Ether will be rapidly ozonized by the Pyroxyline (p. 104). A cool cellar or cupboard will answer the purpose.

On adding the iodizer to the plain Collodion, no immediate change of colour ought to result, except in very hot weather, or in the case of plain Collodion which has been long kept. By the following day, *a straw-yellow* tint may be expected; in a fortnight, a full yellow; and in a month, a brown tint. These changes, however, will vary with the purity of the Ether, and with the temperature.

THE NITRATE BATH.

This solution is the same as that given for Positives at page 279, *Acetic Acid* however being used in acidifying instead of Nitric Acid. Very good Positives can be taken in the Bath prepared for Negatives, if the Collodion contains Bromide, and has a yellow colour from free Iodine. Take of—

Recrystallized Nitrate of Silver .	30 grains.
Glacial Acetic Acid	$\frac{1}{5}$ minim.
Alcohol	15 minims.
Distilled Water	1 fluid ounce.

In the Vocabulary, Part III., directions are given for the purification of Nitrate of Silver ; also for the testing of distilled water, and the best substitutes when it cannot be obtained.

When bromo-iodized Negative Collodion is used, in preference to the simply iodized Collodion, the sensitiveness and intensity will both be increased by using forty grains of Nitrate of Silver instead of thirty grains, the proportions of the other constituents remaining the same.

The Bath must be saturated with Iodide of Silver, and Nitric Acid neutralized if it be present. Weigh out the total quantity of crystals of Nitrate required for the Bath, and dissolve in about twice their weight of water. Then take a quarter of a grain of Iodide of Potassium to each 100 grains of Nitrate, dissolve in half a drachm of water, and add to the strong solution ; a yellow deposit of Iodide of Silver first forms, but on stirring is completely redissolved. When the liquid is clear, test for free Nitric Acid by dropping a piece of blue litmus-paper into the strong solution. If at the expiration of two minutes the paper appears *reddened,* Nitric Acid is present, to neutralize which add a few drops of solution of Carbonate of Soda (10 grains, more or less, to the ounce of water) until a distinct turbidity, remaining after agitation, is produced. Then dilute down the concentrated solution with the remaining portion of the water, stirring all the time, and filter out the milky deposit. If the liquid does not at first run clear, it will probably do so on passing it again through the same filter.

Lastly, add the Acetic Acid and the Alcohol to the clear filtered liquid. The object of the Alcohol is to accelerate the process of sensitizing, by making the film take the Bath more quickly.

Some employ Ammonia for neutralizing the Nitric Acid contained in the crystals, but by so doing *Nitrate of Ammonia* is formed, and the Bath in consequence dissolves the excess of Oxide of Silver, and remains very alkaline after filtering.

Bear in mind that all the common metals decompose Nitrate of Silver, and consequently that the Bath must be kept in glass or porcelain, out of contact with iron, brass, etc.

The Writer finds that the Bath does not become weakened by use to the extent that would be anticipated. Very rarely does the cover of the trough fit tight enough to prevent all evaporation, and consequently it is sufficient in most cases to fill up as it becomes exhausted, with a fresh portion of the same; or with a thirty-five grain solution of Nitrate of Silver. To be continually adding crystals of Nitrate is an error, and is likely to favour staining and excessive density of image.

Negative Baths are generally laid aside from having acquired the property of giving streaky films. This results from the accumulation of Ether and other organic matters as the Bath becomes very old, and it is then better to begin afresh and prepare a new one.

The Writer, as will be seen from Part I. (p. 133), disapproves of dropping Ammonia into old Baths to remove Nitric Acid, or of shaking them up with chalk for the same purposes; being convinced that fewer failures would occur if the plan were generally followed of using pure Collodion, and never interfering with the Bath.

THE DEVELOPING SOLUTIONS.

FORMULA No. 1.

Pyrogallic Acid	1 grain.
Glacial Acetic Acid	20 minims.
Distilled Water	1 ounce.

FORMULA No. 2.

Pyrogallic Acid	1½ grain.
Citric Acid	¾ grain.
Alcohol	20 minims.
Water	1 ounce.

FORMULA No. 3.

Sulphate of Iron	12 grains.
Glacial Acetic Acid	30 minims.
Distilled Water	1 ounce.

Remarks on Formula 1.—This is the form commonly employed, and will seldom require any modification; in cold and damp weather, however, if the Negative should develope slowly and be wanting in bloom and depth, reduce the Acetic Acid to ten minims and increase the Pyrogallic Acid to 1½ grain. No filtering of this solution will be required as a rule.

Read the articles "Water," "Acetic Acid," and "Pyrogallic Acid," in the Vocabulary.

Sometimes an addition of twenty minims of Alcohol to the ounce of developer will be an improvement, when, from age of the Bath and accumulation of Ether the solution flows over the film in an oily manner. It is better, however, to dispense with the Alcohol if possible.

If the solution of Pyrogallic Acid be kept for a few days, it becomes yellow. In this state it will still develope the picture, but is apt to produce a feeble Negative, and to discolour rapidly on touching the film.

Remarks on Formula 2.—Useful in very hot weather for objects well lighted (p. 163), or in the case of Collodion which solarizes the sky and gives a red picture. The Pyrogallic Acid and Citric Acid may be weighed out and carried in packets ready mixed for a journey, but the solution loses a great part of its reducing power after keeping for a few days. No filtering needed as a rule.

Remarks on Formula 3.—In mild weather the proportion of the Iron salt may be reduced to ten grains. The large quantity of the Acetic Acid renders the employment of Alcohol unnecessary. Six grains of crystallized Acetate of Soda are added by some operators, to increase the intensity. No filtering needed.

THE FIXING SOLUTION.

Take of Hyposulphite of Soda . . .	4 ounces.
Common Water	4 ounces.

Dissolve the crystals in the Water with or without the aid of heat. No pulverizing or filtering will be required. Use the liquid over and over again until it becomes exhausted, when it may be thrown away. Traces of the Pyrogallic Acid from the Negatives soon discolour the fixing solution, but this is immaterial.

If a jug be employed to hold this liquid, it must be made of good ware, or the Hyposulphite will pass through and form an efflorescence on the exterior. As a rule, no vessel in which solution of Hyposulphite has been long kept ought to be employed for any other purpose.

VARNISH.

It is of the greatest importance to use a Varnish which will not crack, and one of considerable body, so as to protect the Negative in the printing process. The Writer selects the following as the best Varnish of which the formula has been given to the public:—

Alcohol of ·815	40 ounces.
White Stick Lac	3 ounces.
Picked Sandrac	3 drachms.

Place in a flask, and raise the temperature by plunging the flask into hot water, and in a few minutes the solution will be effected, with the exception of a few light filaments of insoluble lac. Filter through bibulous paper, and the light-yellowish liquid will be fit for use.

Warm the Negative *gently* (to 140° or 160°) before a fire, and pour the Varnish on and off, like Collodion. If the glass be made too hot, it will be difficult to apply the Varnish, and it will also dry very rapidly, producing veins. Never attempt to give a second coating, as the Negative would then inevitably be spoiled.

These particulars are given on the authority of Monckhoven.

CHAPTER II.

MANIPULATIONS AND PROCESSES.

The contents of this Chapter may be arranged in seven distinct Sections.

Section I.—Ordinary Manipulations of the Collodion Process.
Section II.—Positive and Negative Portraiture.
Section III.—Landscape Photography.
Section IV.—Copying Works of Art, etc.
Section V.—Stereoscopic and Instantaneous Pictures.
Section VI.—Micro-Photography.
Section VII.—Photography in hot climates.

SECTION I.

Manipulations of the Collodion Process.

These include the cleaning of the plates, coating them with Collodion, exposing in the Camera, developing, fixing, and varnishing.

CLEANING THE GLASS PLATES.

Care should be taken in selecting glass for Photography. The ordinary window-glass is inferior, having scratches upon the surface, which often cause an irregular action of the developing fluid; and the squares are seldom flat, so that they are apt to be broken in compression during the printing process.

The patent plate answers better than any other description of glass, especially for large sizes; but if it cannot be procured, the "flatted crown glass" may be substituted.

Before washing the glasses, each square should be roughened on the edges and at the corners by means of a file or a sheet of emery-paper; or more simply by drawing the edges of two plates across each other. If this precaution is omitted, the fingers are liable to injury, and particles of flue are cut from the cloths used in wiping. When the Collodion is at all of a contractile nature, the *surface* of large plates should be roughened as well as the edges, to prevent the film from drawing itself away, and allowing the fixing solution to pass beneath. Place the glass upon a cloth at the end of a table, and rub it sharply with a piece of soft stone, sold for whetting scythes. A groove will soon be formed in the stone, and both the edge and the surface of the glass will be roughened at the same time, the latter to the extent of $\frac{1}{8}$ inch all round.

In cleaning glasses, it is not sufficient, as a rule, to wash them simply with water. This may be proved by putting the glass under a tap, and observing how the fluid runs off from the surface without wetting it, showing the presence of *grease*, or other organic impurity. A cream of Tripoli powder and Spirits of Wine, with a little Ammonia added, is commonly employed. A tuft of cotton is to be dipped in this mixture, and the glasses well rubbed with it for a few minutes. They are then rinsed in plain water and wiped with a dry cloth. Do not rear them up on end to dry spontaneously, because the evaporation would leave a film upon the surface, and *dust* might rise by capillary attraction from the table on which they were standing.

The cloths used for cleaning glasses should be kept expressly for that purpose; they are best made of a material sold as fine "diaper," and very free from flocculi and loosely-adhering fibres. They are not to be washed *in soap and water*, but always in pure water or in water containing a little Carbonate of Soda. Never lay these cloths upon the operating table, but place them when not in use across the back of a chair, or in a bag kept for the purpose. If the hands are warm, wear a pair of gloves, that the cloths may be kept clean.

After wiping the glass carefully, complete the process by polishing with an old silk handkerchief, avoiding contact with the skin of the hand. Some object to silk, as tending to render the glass electrical, and so to attract particles of dust, but in practice no inconvenience will be experienced from this source. Leathers may be used instead of silk for the final polishing; they must be first beaten, then washed in pure water, dried in the sun, and well pulled out, until they are soft and yielding.

Before deciding that the glass is clean, hold it in an angular position and *breathe* upon it. The importance of attending to this simple rule will be at once seen by referring to the remarks made at page 50. Stow the cleaned plates away in grooved boxes; the plan of packing them between sheets of paper, as is sometimes done, is not to be commended, since the letters and marks upon the paper are gradually impressed upon the glass.

Other modes of cleaning glasses have been recommended, of which, perhaps, the use of residues of Collodion is the most simple. Add a fluid drachm of Water to the ounce of Collodion, until the Pyroxyline begins to form a white deposit, not redissolved on agitation; this will prevent the Collodion from evaporating too quickly. Then pour a little upon the glass, and rub with a tuft of wool or a piece of cambric. Clean off with a second piece, and finish with cloth and leathers, as before: no water will be required. The simplicity of this plan is its recommendation, and it answers remarkably well. The Ether in the Collodion removes the grease, although Alcohol, sometimes advised in preference, does not always do so.

Caustic Potash, sold by the druggists under the name of "Liquor Potassæ," is very efficacious in cleaning glasses; or in place of it, a warm solution of "washing Soda" (Carbonate of Soda). Liquor Potassæ, being a caustic and alkaline liquid, softens the skin and dissolves it; it must therefore be diluted with about four parts of water, and applied to the glass by means of a cylindrical roll of flannel. After wetting both sides thoroughly, allow the glass to stand for a time until several have been treated in the same way; then wash with water and rub dry in a cloth. Observe in adding either Potash, Carbonate of Soda, or Ammonia to common hard Water, that a deposit of *Carbonate of Lime* may be formed. In that case if the glasses are left in the liquid, they will soon be covered with little crystals, which adhere tightly. Cyanide of Potassium, which some employ as a cleansing agent, will also precipitate Lime salts from hard water, since it is almost invariably contaminated with Carbonate of Potash.

New glass plates are frequently dotted on the surface with little gritty particles, which consist, as above, of Carbonate of Lime. They are not removed by Potash or any alkali, but dissolve readily in a diluted acid, such as Oil of Vitriol with about four parts of water added, or dilute Nitric Acid.

The objection to the use of Nitric Acid is, that if allowed to come in contact with the dress, it produces stains which cannot be removed unless *immediately* treated with an alkali. A drop of Ammonia should be applied to the spot before it becomes yellow and faded.

After a glass has once been coated with Collodion, it is not necessary in cleaning it a second time to use anything but pure water: but unless the cloths are scrupulously clean, it will be a safe precaution to finish off with old Collodion, since soiled cloths applied to a wet glass usually impart some impurity. The habit of washing off failures at the time should however by all means be acquired, as it will save a great deal of trouble and annoyance from dirty glasses.

When glasses have been repeatedly used in Photography, they often become at length so dull and stained, that it is better to reject them.

In the Positive glass process the Iron Salts used in developing sometimes leave red stains which alkalies will not touch. Dilute half an ounce of Nitric Acid with a quart of water, and leave the plates in the liquid twelve hours. Oxides of Iron are also soluble in dilute Muriatic or Sulphuric Acid.

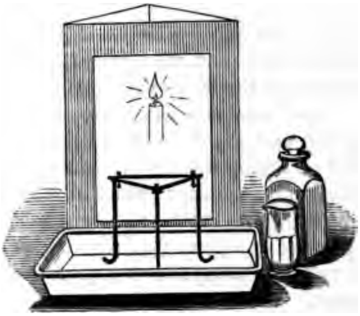
General remarks.—Amateurs often waste time in needlessly rubbing and breathing upon glasses, the only result of which is to render them warm and electric, so that the Collodion will not adhere. Particles of saliva are also projected upon the glass, and being imperfectly removed by the leather, produce transparent markings, like the barb of a feather. The condition of the cloths is commonly too much neglected; they are thrown down, and continually handled with warm hands. Hence no sooner is one mark rubbed off than another makes its appearance. Cleaning should be done with a quick and light movement, such as the cabinet-maker uses in polishing; and in the case of plates of a large size a screw press should be used to give a firm purchase. If possible, leave the glass for a short time after cleaning it, and before pouring the Collodion.

COATING THE PLATE WITH THE COLLODION.

How to prepare the dark room.—The two operations to be performed in the yellow room, are the sensitizing and the development of the plates. The fixing however may be done in open daylight, and perhaps it is better so; since there is a great chance of confusion, when many bottles and solutions are crowded together.

In some convenient part of the room place a table, with the Nitrate Bath on one side and a tray for developing on the other; a candle shielded by yellow calico standing in the centre. These two solutions—the Bath and the developer—ought never to be placed side by side, otherwise the blotting-paper which is used would become saturated with the wrong liquid and spoil the pictures. Have at hand also a supply of water and two or three cloths; one for wiping the fingers after sensitizing, and the other after developing.

Beginners often fail from the developing room admitting white light, and therefore the Writer advises that in the first trials the room should be made so dark that the hand cannot be seen before the face, and afterwards illuminated by means of a lamp or candle screened with yellow glass. The following description of a Photographic Lantern is extracted from Professor Delamotte's pamphlet on the 'Oxymel Preservative Process':—"Take three millboards, about twelve inches high by nine inches wide, and cut out a large piece, say eight inches by five inches, from the centre of each. Lay all three boards close together, side by side, and having dabbed on paste or glue, cover them entirely with two thicknesses of yellow calico. Ornament them in any way you please on the other side. When set up so as to form a triangle, with the calico side inwards, a candle may be placed in the centre, and when not in use, the lantern will fold up and make a good portfolio for paper, etc."

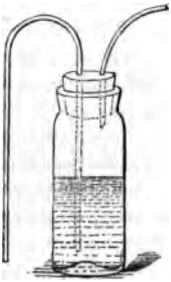


Before commencing work, ascertain that the light is sufficient to enable you to see easily, otherwise it will be difficult to apply the developer evenly to the film.

Coating the Plate.—The Collodion may, as a rule, be iodized some hours before use, in order to allow time for a little change of colour, but sometimes it is convenient to iodize and use it immediately, which can generally be done successfully, although extra cleanliness will be required in such a case to avoid the occurrence of white spots. The graduated Collodion-pouring-glasses sold in the shops are usually made tall and narrow: but the Writer uses a wide-mouthed stoppered bottle, and makes a scratch on it with a three-cornered file at a point corresponding to the measure for the iodizing liquid, viz. one quarter of the entire bulk.

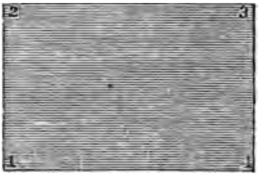
Before coating the plate with Collodion, see that the fluid is perfectly clear and transparent, and that all particles have settled to the bottom; also that the neck of the bottle is free from hard and dry *crusts*, which, if allowed to remain, would partially dissolve and produce striæ upon the film. Before taking the first picture, pour out a few drops of Collodion on the floor; this will remove stray particles, and clear the way for the remainder.

A useful piece of apparatus for decanting Collodion containing undissolved Pyroxyline is represented in the following woodcut.



The Collodion, having been iodized some hours previously, is allowed to settle down in this bottle; then by gently blowing at the point of the shorter tube, the small glass siphon is filled, and the fluid drawn off more closely than could be done by simply pouring from one bottle to another. An apparatus for the same purpose, but contrived so as to fit any bottle, may be made by passing the two tubes through *a larger cork* than that above shown, and then pressing down the lower surface of this cork upon the open neck of the bottle.

When the Collodion is properly cleared from sediment, take a glass plate, previously cleaned, and wipe it gently with a broad camel's-hair brush, in order to remove any particles of dust which may have subsequently collected. If it be a plate of moderate size, it may be held by the corners in a horizontal position, between the forefinger and the thumb of the left hand. The Collodion is to be poured on steadily until a circular pool is formed, extending nearly to the edges of the glass.



By a slight inclination of the plate the fluid is made to flow towards the corner marked 1, in the above diagram, until it nearly touches the thumb by which the glass is held: from corner 1 it is passed to corner 2, held by the forefinger; from 2 to 3, and lastly, the excess poured back into the bottle from the corner marked No. 4. It is next to be held over the bottle for a moment, until it *nearly* ceases to drip, and then, by raising the thumb a little, the direction of the plate is changed, so as to give a rocking movement, which makes the diagonal lines coalesce and produces a smooth surface. The operation of coating a plate with Collodion must not be done hurriedly, and nothing is required to ensure success but steadiness of hand and a sufficiency of the fluid poured in the first instance upon the plate.

In coating larger plates, the *pneumatic* holder, which fixes itself by suction, will be found the most simple and useful.

The presence of white light in the room does no injury until the plate has been placed in the Bath, and therefore the door may remain open during the operation of coating, since it would be difficult to apply the fluid evenly without plenty of light. Draughts from an open door must, however, be avoided, as promoting too rapid evaporation. If the light of a candle is employed in coating, let the wick burn long and smoky, to produce a yellow flame; also be careful not to bring the glass too near, and especially not to hold it *above* the flame, or the vapour of the Ether will fall and the whole will be in a blaze (p. 274).

The common error in coating glasses is to keep the eye too much upon the neck of the bottle, and not sufficiently upon the glass. The pool of Collodion is itself the guide to the right position of the plate, and if it begins to flow away to one corner, that corner is the lowest, and must be raised a little. Apply the whole quantity of Collodion first and incline the plate afterwards; but never tilt and pour at the same time. Do not be economical as regards quantity, and if a little should flow away at the edges it will be of no consequence.

Sensitizing the Film.—Examine first the state of the Bath solution. This liquid is most conveniently kept in a glass trough mounted in a wooden box, with a loosely-fitting cover. It is an advantage to leave the Bath always in the trough, that it may settle down and clear itself after the day's work is done; but if the plan of keeping it in a separate bottle be adopted, remember to wash out the trough with water, and drain it before putting in the Nitrate solution; otherwise there will be dust and scum upon the surface when it is again filled. Porcelain troughs are sometimes used, but they should be glazed with extra care, or the Nitrate of Silver will percolate through to the exterior.

Begin by bringing the Bath out to the light for an instant, and examining the surface. If there be any greasy scum, remove it carefully with blotting-paper. In using a new sample of Collodion, ascertain that it does not leave a floating film of Iodide upon the surface of the Nitrate in dipping, which often happens with over-iodized Collodion, deficient in setting qualities.

Lastly, arrange the Bath upon layers of clean blotting-paper for draining, and all will be ready for immersion.

With regard to the time which ought to elapse between coating and dipping, observe the following:—After exposing a layer of Collodion to the air for a short time, the greater part of the Ether evaporates, and leaves the Pyroxyline in a state in which it is neither wet nor dry, but receives the impression of the finger without adhering to it. This is termed *setting*, and when it takes place, the time has come for submitting the plate to the action of the Bath.

If the film be lowered into the Nitrate before it has set, the effect is the same as that produced by adding *Water* to Collodion. The Pyroxyline is precipitated in part, and consequently there are cracks at the lower edge of the plate: the film is also easily loosened, and is very liable to wrinkle at the bottom part. On the other hand, if it be allowed to become too dry, the Iodide of Silver does not form perfectly at the top of the plate, and the film, on being washed and brought out to the light, exhibits a peculiar iridescent appearance, and is paler in some parts than in others: pictures taken on a film of this kind are always weak, and lie very much upon the surface of the Collodion.

No rule can be given as to the exact time which ought to elapse before dipping: it varies with the temperature of the atmosphere, and with the proportions of Ether and of Pyroxyline; thin Collodion containing but little Alcohol requiring to be immersed more speedily. Twenty seconds in the common way, or ten seconds in hot weather, will be found an average time. The correct mode of proceeding is to make a trial with the first plate coated, and not to dip it until you find by the touch that the lower corner has become firm and solid.

When the plate is ready, rest it upon the glass dipper, Collodion side uppermost, and lower it into the solution by a slow and steady movement; if any pause be made, a horizontal line corresponding to the surface of the liquid will be formed. Then place the cover upon the vertical trough and darken the room, if this has not already been done.

Whilst the plate remains in the Bath, the operator may occupy himself in wiping out the corners and lower edge of the slide with blotting-paper; next, in measuring a sufficiency of the developing solution, and in focussing the object. Then dip the fingers an instant in water, to cleanse them from any traces of Pyrogallic Acid, and return to the Bath.

The light ought to fall upon the plate at a sharp angle whilst it is lifted from the Bath, that the operator may see the greasy lines upon the surface. An immersion of a minute to a minute and a half will usually be sufficient; or two minutes in cold weather, and with Collodion containing but little Alcohol. Something will depend upon the number of times the plate is moved up and down, and many adopt the plan of leaving it in five minutes, and then taking it out without any movement. When the liquid flows off in a uniform sheet, the decomposition may be considered to be perfect. The principal impediment in this part of the process lies in the difficulty with which Ether and Water mix together, which causes the Collodion surface on its first immersion to appear *oily* and covered with streaks. By gentle motion the Ether is washed away, and a smooth layer obtained.

The normal Collodion of page 262 is subject to the defect of occasional *straight black lines*, taking the direction of the dip in the Bath. They are quite distinct from the wavy lines presently to be mentioned (which are in the direction of the draining), and can only be obviated by giving the plate a to-and-fro movement for the first 30 seconds after it enters the Bath.

When the Bath is in perfect order no harm will result from leaving the plate in it for a quarter of an hour or longer, but sometimes the film will eventually become covered with little projecting crystals, each of which produces a white spot; and in the case of extreme heat of the weather, or of a bath contaminated with organic matter, the longer the film is left in, the greater the chance of fogging. The experience of most practical operators is not in favour of leaving plates in the Bath over two or three minutes.

The plate is next removed from the dipper, and held vertically in the hand for a few seconds upon blotting-paper, to drain off as much as possible of the solution of Nitrate of Silver.* It is then wiped on the back with filtering-paper, and placed in a clean and dry slide, after which it is ready for the Camera.

Success will much depend upon the careful draining of the film, and hence the importance of having the developing room thoroughly darkened, in order to do this efficiently without fear of producing fogging. The older the Bath the greater the care required in draining, because the presence of the Ether gives a tendency to run into narrow lines and channels upon the surface of the film. Especially avoid *altering the direction of the plate after draining* and previously to putting it into the slide. In the case of Stereoscopic glasses the direction of the film is often so changed, and consequently there are lines on the lower picture, from the wave of the Nitrate altering its course. Transparent curtain markings at the bottom of the film, and a blurring of the image downwards, are also defects likely to follow imperfect draining.

The Writer objects to another change of direction which is sometimes given to the plate, viz. a complete turn on taking it out of the Bath, so as to bring the top edge downwards on the blotting paper. This is a fruitful source of stains, since it is very difficult to drain away the excess of Nitrate under such circumstances.

The amateur is advised not to proceed to the process of taking pictures in the Camera until, by a little practice, he is able to produce a perfect film, which is uniform in every part and will bear inspection when washed and brought out to the light.

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* This blotting-paper must be frequently changed, or stains will be produced at the lower edge of the plate during the development.

Such a film may be expected to present the following appearance:—Smooth and uniform, both by reflected and transmitted light; free from crapy lines, such as would be caused by not rocking the plate properly whilst coating it, and from opaque dots due to small particles in suspension: also from marginal thickenings of the Iodide, which may result from the neck of the bottle not having been drawn along the lower edge of the glass whilst the Collodion was setting.

The evidences of a too rapid immersion in the Bath are sought for on the side of the plate from which the Collodion was poured off. This part remains wet longer than the other, and always suffers the most. On the other hand, the upper part of the plate must be examined for the pale colour or the zigzag markings characteristic of a film which had become too dry before immersion, since the Collodion is thinner there than at any other point.

EXPOSURE OF THE PLATE IN THE CAMERA.

The proper time for exposure will depend upon the kind of picture to be taken, and directions on that head must be sought in the Second and following Sections of this Chapter. Although perfect cleanliness is very essential to success, yet the Camera and apparatus ought not to be wiped out immediately before use, as the effect of doing so would be to stir up dust: the cloth employed may also be slightly damped with advantage. Examine the Lens and see that the glasses are free from cobweb markings, and from condensed moisture.

After the plate has been taken out of the Bath, it should be exposed and developed with all convenient despatch; otherwise the film will become partially dry, the developing solutions will not flow easily, and the Negative will be weak and metallic. There are often white spots upon plates long kept, from small particles of dust, etc., becoming centres of chemical action.

Whilst focussing the object, place the slide *gently* on the ground, wrapped up in a black cloth, and be careful to keep the same side always downwards.

THE DEVELOPMENT OF THE IMAGE.

The details of this part of the process differ so much in the case of Positive and Negative pictures, that it will perhaps be better to confine ourselves to the latter, and to defer the consideration of the development of glass Positives until the next Section.

On taking the plate out of the slide there will be some accumulation of Bath solution at the lower edge, which, if the glass be held flat in the hand for a short time, will be seen to work its way along the surface of the film; and the effect will be to produce *a transparent* mark on applying the Pyrogallic Acid. To prevent this annoyance, the film may be placed vertically on absorbent blotting-paper, and the liquid drawn off by suction.

The Pyrogallic Acid solution having been previously measured out (about three drachms for a stereoscopic plate or a plate 5×4, one ounce for a 9×7, and twelve drachms for a plate of 10×8), hold the glass in the hand in the same manner as when coating it with Collodion, and throw the liquid on evenly. It must not be poured from a height on to one single spot, or the whole of the Nitrate of Silver would be displaced from that spot, leaving a transparent mark of non-reduction. The lip of the developing glass should be depressed until it nearly touches the film, so as to apply the liquid close to the edge of the plate, or to some part of the image which is of minor importance. Always pour out the whole of the measured quantity of developer, and then move the plate so as to keep it waving backwards and forwards upon the film. It will be quite necessary to have the source of light so arranged that it falls nicely upon the Collodion surface, because the operator has to tilt the glass until the developer runs into each of the corners, and to keep his eye upon the wave as it moves backwards and forwards, in order to prevent it from flowing off at the edges of the plate, or trickling down his sleeve.

The freedom with which the developer flows depends much upon the Collodion, and the length of time it was held before dipping, since if the film retain too much Ether, it will repel aqueous liquids. Also it depends upon the Bath in a measure, for when this solution is newly mixed, and comparatively free from Alcohol, it will be sometimes necessary to give the plate a sudden *jerk*, to prevent the Pyrogallic Acid solution from stopping short of the edge.

Notice whether the developer remains bright and clear, or becomes turbid before the image is fully brought out. In the latter case the heat is too high, or the Chemicals are in fault, and the Chapter on "Failures" must be consulted.

Watch the course of the development for about thirty or forty seconds, and especially the behaviour of those parts of the film which at first remain yellow, but at length begin to evolve fine details corresponding to the shadows. Keep the Pyrogallic Acid on the plate until nothing more appears in these yellow parts, and then pour it off into a measure, and hold the plate for an instant against the light, so as to look through it and see the appearance of the Negative image.

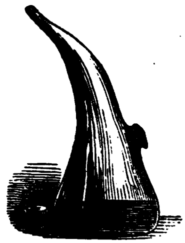
At this point a failure very commonly occurs, from the operator being too tardy in his movements, and allowing the developer to run into oily lines, so as to produce diagonal black streaks upon the film.

Having decided that the image is sufficiently intense, proceed to the fixing: but if it appears too weak (and allowance must be made for the lowering action of the Hyposulphite), carry the development into the second stage. To do this, pour away the discoloured Pyrogallic Acid, and wash out the glass rapidly with water; then measure out a fresh portion, add to each drachm about five drops of a 20-grain solution of Nitrate of Silver, and apply it a second time to the film, until the desired intensity is obtained.

It is not recommended to add a few drops of the Nitrate Bath to the Pyrogallic Acid, but to employ a weaker solution of Nitrate of Silver, not saturated with Iodide. This Nitrate of Silver must also be very pure, or the developer will soon discolour and the shadows become stained.

As *time* ought to be economized as much as possible, observe the following:—If the image is well out before the Pyrogallic Acid becomes turbid, it will be unnecessary to throw away the first portion, but any amount of strengthening may be obtained by pouring the same developer back into the measure, and adding the Nitrate of Silver. Neither is it necessary to wash out the developing glass with water when it contains Pyrogallic Acid *simply discoloured,* but anything approaching *turbidity* will suggest an immediate change of solution, and a washing with water, both of the film and the glass. The addition of fresh Nitrate of Silver to a developer in such a state, is improper: the Silver then falls irregularly, and the chance of staining is increased.

With regard to the quantity of Nitrate of Silver to be added to the developer, nothing positive can be stated. At least three times more will be required in cold than in hot weather, and something will depend upon the condition of the developer itself. The rapidity of discoloration or turbidity in the Pyrogallic Acid is the proper guide to follow; and the two liquids may be mixed even in equal bulks if it is found that the mixture remains clear for twenty or thirty seconds, so as to give time for pouring it over the image. As a rule however the less the quantity of Silver in proportion to the Pyrogallic Acid the better.



The accompanying diagram shows the best form of dropping-bottle for Nitrate of Silver that the Writer has seen.

The bottle being partially full of solution, incline it gently, when the air will pass in at the wide mouth, and the liquid will drop out at the fine-drawn end. In travelling both orifices are closed with corks.

Development with Sulphate of Iron.—This reducing agent developes the picture so rapidly when the Collodion contains only Iodide, that its employment requires care. The solution should be thrown on to the plate rather quickly, and with a sweep. In the course of a few seconds the image appears in all its parts, and the liquid on the film shows signs of commencing turbidity. When this happens, the developer must be poured off immediately, and the plate washed with water, otherwise the shadows will be misty from adherent particles of Silver.

Collodion containing Bromide developes in a more gradual manner than the simply iodized, and the Sulphate may be kept longer upon the film without any danger of producing fogging. The condition of the shadows will indicate the correct time, for if the Sulphate be too soon removed, there will remain much of the yellow Iodide, leaving bare glass after fixing.

Plates developed with Sulphate of Iron are rarely sufficiently intense in the first instance: They may be further blackened by washing the film and pouring over it a twenty-grain solution of Nitrate of Silver, followed by a second application of Sulphate of Iron. A better process however is to wash away all traces of the Iron salt by a stream of water applied for a few seconds, and then to mix the ordinary solution of Pyrogallic Acid with Nitrate of Silver, and proceed as described in the last page.

Appearance of the Negative image as a guide to the exposure to Light.—An under-exposed plate developes slowly. By continuing the action of the Pyrogallic Acid, the high lights *become very black*, but the shadows are usually defective, nothing but the yellow Iodide being seen on those portions of the plate. After treatment with the Hyposulphite, the picture shows well as a Positive, but by transmitted light all the minor details are invisible; the image is black and white, without any half-tone.

An over-exposed Negative developes rapidly at first, but soon appears to blacken slightly at every part of the plate. After the fixing is completed, the image is indistinct, and very little can be seen by reflected light but a uniform grey surface of metallic Silver. By transmitted light the plates often show a red or brown colour, and the image is *faint* and flat. The half-shadows having acted so long as nearly to overtake the lights, there is a want of proper *contrast;* hence the over-exposed plate is the exact converse of the under-exposed, where the contrast between lights and shadows is too well marked, from the absence of intermediate tints.

A Negative which has received the proper amount of exposure, usually possesses the following characters after fixing:—The image is partially but not fully seen by reflected light. In the case of a portrait, any dark portions of drapery show well as a Positive, but the features of the sitter are scarcely to be discerned. By transmitted light the figure is bright, and appears to stand out from the glass: the dark shadows are clear, without any misty deposit of metallic Silver; the high lights black *almost* to complete opacity.

Collodion with strong organic reactions (p. 155) gives a Negative which often shows upon the surface of the glass nearly as well as by transmission. And if the light be at all good, the yellow creamy appearance which Photographers term *bloom* ought to be seen upon the image. Its absence in the case of a simply iodized Collodion, not containing Bromide, usually implies that some of the chemicals are out of order.

Fixing and varnishing the Negative.—Wash the film gently with water and pour the solution of Hyposulphite on and off until the whole of the Iodide has been cleared away. The solution of Hyposulphite becomes nearly black after a time, but this is of no importance, some operators considering that even a preliminary washing to remove the Pyrogallic Acid solution is unnecessary. A thorough washing after the Hyposulphite will be essential, and it is from neglecting this point that beginners frequently find their plates covered with crystals on drying. Even supposing the washing to have been sufficient to prevent the occurrence of crystallization, there may yet be a blueness and loss of intensity at the lower part of the film, visible after drying, from traces of Hyposulphite remaining in the Collodion, and when such is the case, the varnish does not always adhere properly, but spirts out when applied to the heated plate, leaving minute holes. These Negatives generally absorb atmospheric moisture and remain continually damp, fading away after a time from the edges towards the centre.

The proper mode of washing is as follows:—If a tap is at hand, turn it gently and allow the water to flow in a stream upon the centre, inclining the plate so that it runs off from each of the corners in succession; continue this for two or three minutes, when the Hyposulphite may be considered as removed. If running water cannot be had, first wash off the excess of the fixing agent by water poured from a jug, and then lay the plate film upwards in a dish and leave it for three or four hours, giving several changes of water. When the Collodion appears to be tender, and inclined to separate from the edges, see that the liquid is made to flow *away* from the glass at that point, so as to keep the film down and prevent the water from passing beneath. This observation applies in a still more decided manner to the Hyposulphite, because if the fixing solution once works beneath the film, it cannot afterwards be got out, and the Negative will lose intensity on drying.

After the Negative has been washed, stand it on clean blotting-paper to dry; otherwise dust will ascend the film by capillary action, and give an appearance as if impurities had drained down from above.

It is important that the plate should be dried by artificial heat before varnishing, and the Negative will also look more neat if a damp cloth be first run along the edge with the finger and thumb, so as to scrape away the Collodion and leave a clear margin of an eighth to a quarter of an inch all round. After doing so, remove with the nail or a camel's-hair brush any loose or detached particles of Collodion, which otherwise might be washed on to the image by the varnish and produce a spot.

SECTION II.

Portraiture—Positive and Negative.

We commence this Section by remarking upon the advantages or the contrary to be expected from the use of a glass house in Collodion Portraiture; adding at the same time a few hints on the mode of its construction. Those who are accustomed to work beneath glass, are often at fault on trying to take a picture in the open air, and obtain under such circumstances a hard and unpleasing portrait, with exaggerated contrast of light and shade. It is, without doubt, somewhat difficult to secure fine gradation of tone when the object is brilliantly illuminated, on account of the actinic power of the Lenses which are employed in portraiture; and therefore, unless the Chemicals are prepared purposely, the subdued light of a glass studio is likely to give the best effect.

The mistake often committed in constructing glass houses, is to use the common window-glass for glazing. This glass has usually a green tint, and when exposed for many months to the air often undergoes a further change, by which the photographic rays are absorbed. The Writer, in working in the glass studios of various operators, has been surprised at the difference in the time of exposure required, independently of the amount of light admitted. He is therefore of opinion that a very pure white glass should be chosen, and if economy is to be studied, a saving may always be effected by taking the second quality, as it is termed, differing only from the other in the presence of an occasional bull's-eye or flaw.

The glass room which the Author himself has used faces north and south, and is 25 feet long by 12 feet wide and 11½ feet high in the centre, the developing room being placed at the north end. The objection to this arrangement, however, is that when the sun shines, a very perfect system of blinds is required, and a considerable stippling of glass between the blinds to prevent marks on the background. All these inconveniences would be in great measure avoided by making the sitter face the north instead of the south.

It is not necessary to glaze the room quite down to the ground, and black curtains must always be at hand to darken one side when required. The roof overhead may also be opaque to a distance of about six feet from the background, since a vertical light is not allowed. A deal platform of about a foot in height is placed at one end, in order to raise the sitter and obtain a better illumination.

The background may be varied according to the taste of the operator, but to produce a neutral tint, the colour should be something that of common brown paper. Unless, however, the surface is quite dead, the effect of the background will depend upon the amount of light which shines upon it, so that it will produce a different colour in the open air from that given in the glass house.

Proper ventilation is of the utmost importance, the heat being excessive in the summer months.

The developing room is frequently made smaller than is advisable, the consequence of which is that it becomes almost unbearable in hot weather. It ought also to be more generally known that the vapour of Ether, when continually inhaled, has an extremely depressing effect upon the nervous system.

In arranging the sitter, a quantity of black, blue, and white Calico should be at hand. The light, as before said, must not come down directly from above, or it will fall upon the hair so as to make it appear grey, and will also give strong shadows beneath the eyes. A *horizontal* light destroys the shadows entirely and is suitable in the case of deep sunken features, but a light falling *obliquely* from above, and striking more upon one side of the face than the other is the best in the majority of cases.

In order that the eyes of the sitter may not be fatigued, black Calico must be hung in such a way that he may be able to look into a dark corner.

Mr. Keith, of Liverpool, from whose written instructions on the mode of constructing a glass house the Writer has derived advantage, advises that in taking Collodion Positives a very subdued light should be used. In his experiments he proceeded to paste brown paper, first on one square of glass and then on another, until he succeeded in obtaining a soft picture. The state of the Chemicals will influence the result in this particular, although all Positive glass operators are agreed that the middle tints are better preserved when the face and hands of the sitter are shielded from too bright a light, and when reflecting surfaces of white Calico, etc., are laid upon the ground so as to throw back the light into the shadows. In a full blaze of sun, dark drapery often comes out too light to give an agreeable effect (see p. 87).

Directions for working in the open air.—When a glass house is not at command, portraits may be taken in the open air by observing the following precautions:—Always back up the sitter if possible by a dark ground, not less than seven feet square, to prevent diffused light from entering the Lens. To make an effective screen, construct in the first instance a strong deal framework, consisting of a central portion, with two lateral ones hinged to it. Cover the whole with oil-cloth, painted of a suitable colour, and as free from gloss as possible. By bringing one of the two sides forward, you are enabled to throw a shadow on the face of the sitter, and by turning the other side back the whole arrangement may be fixed, and rendered firm. Probably a screen will be required above to cut off the vertical light: and if so, the apparatus may be still further strengthened by constructing this part of a deal framework made to bolt down against the side which projects forward.

When everything is complete, stand in front of the Lens and look in through the glasses from below upwards, to see if there be any reflection from the sky, or other bright objects. Unless the Lens be placed very near indeed to the sitter, it is almost certain that there will be something of this kind, and if so a foggy picture will result. A large funnel of cardboard, linéd with black velvet, should in such a case be carried out to a distance of about a foot in front of the Lens, and the mouth of this funnel should be contracted as far as possible until it begins to cut off the corners of the field. This will render the image very clear, and will wonderfully improve the quality of the picture. Before exposing the plate throw a black silk handkerchief over the end of the funnel, which will be found sufficient to exclude the light.

It is on account of the size of the glasses in a portrait combination, and the fact of their presenting so large a reflecting surface, that the above precautions are required. If small diaphragms were used, the sitter might be arranged with the open sky for a background without producing fogging.

How to test the correctness of the Camera and Lens.— This point must always be attended to in purchasing a new portrait apparatus; from neglecting it many fail in obtaining pictures equal to what the Lens would yield.

First ascertain that the prepared sensitive plate falls precisely in the plane occupied by the ground glass. Suspend a newspaper or a small engraving at a distance of about three feet from the Camera, and focus the letters occupying the centre of the field; then insert the slide, with a square of *ground glass* substituted for the ordinary plate (the rough surface of the glass looking inwards), and observe if the letters are still distinct. In place of the ground glass, a transparent plate smeared with glazier's putty may be used, but the former is preferable.

Another method, more simple than the last, is to gauge the slide with a strip of card. Begin by inserting a glass plate in the slide, and then lay it down upon the table side by side with the focussing glass. Raise the door of the slide, and having applied a flat rule, measure the exact distance between the edge of the rule and the surface of the glass plate. Now place the rule upon a corresponding portion of the focussing glass, when it will be at once evident whether the two planes coincide.

If the result of these trials seems to show that the Camera is good, proceed to test the correctness of the Lens.—

Take a Photograph with the full aperture of the portrait Lens, the central letters of the newspaper being carefully focussed as before. Then examine at what part of the plate the greatest amount of distinctness of outline is to be found. It will sometimes happen, that whereas the exact centre was focussed visually, the letters on a spot midway betwen the centre and edge are the sharpest in the Photograph. In that case the chemical focus is longer than the other, and by a distance equivalent to, but in the opposite direction of, the space through which the Lens has to be moved, in order to define those particular letters sharply to the eye.

When the chemical focus is the shorter of the two, the letters in the Photograph are indistinct at every portion of the plate; the experiment must therefore be repeated, the Lens being shifted an eighth of an inch or less. Indeed it will be proper to take many Photographs at minute variations of focal distance before the capabilities of the Lens will be fully shown.

The object of finding the point at which the sharpest image is obtained will also be assisted by placing several small figures in different planes and focussing those in the centre. This being done, if the more distant figures come out distinctly in the Photograph, the chemical focus is *longer* than the visual, or *vice versâ* when the nearest ones are most sharply defined.

Mr. Shadbolt has given very lucid instructions for testing a portrait Lens, which the Writer copies by his permission:—

"Put the Lens in its place and test for coincidence of chemical and visual foci as follows: take any paper with a number of *fine* lines drawn upon it, for instance, that upon which patterns are printed for ladies' Berlin wool work, or else some small but clear printed matter, and paste either upon stout cards, with a large distinctive letter or number upon each one: about ten or a dozen will be enough. Place a slip of deal at an angle of 45°, and with a thin saw make a series of cuts perpendicular to the horizon, one behind another, at about an inch distance apart, a card with the printed matter or lines being slipped into each. All will then be visible at once from a single point, just in the same way as would be the case with the faces of a number of people standing one behind another upon a flight of stairs. Now carefully focus for the fine lines or small letters on one of the cards in the *centre* of the group, taking special note at the same time of its distinctive letter or number, and having done so, expose a sensitive plate and develope it. If the card upon which the focus was taken be most distinct and sharp, the *actinic correction* is perfect: if, however, the best definition be upon one nearer to the Lens than that focussed, it is under-corrected; if further from it, over-corrected."

The above directions are abundantly sufficient for testing the Camera and Lens. White light, however, occasionally enters the instrument between the two sliding portions of the body, and this will be seen on throwing a black cloth over the back and looking into the interior. Or some scattered rays may pass in through the chink when the door of the slide is raised. It is therefore customary always to throw a large black cotton velvet focussing cloth over the Camera, and to introduce the arm beneath this cloth whilst opening the slide.

Portrait Lenses *magnify* those parts of the object which are nearest to the glass, and hence the complaints of enlargement of the hands and lower portions of the figure. This must be obviated by placing the sitter nearly in one plane, and sometimes pointing the Lens a little downwards. The Author hears this practice spoken against as theoretically incorrect, but he has often improved his picture by adopting it. It makes the head and forehead a little larger, and diminishes the size of the feet. The figure, in fact, becomes more of a pyramid with the base above.

Swinging backs to portrait Cameras are useful in focussing near and distant parts of the object at one time, supposing the figure to be arranged in a diagonal position with reference to the Lens; but they are very expensive and add much to the bulk of the instrument.

The Lens must be chosen according to the size of picture which is required, always bearing in mind that the smallest Lenses are as a rule the most perfect, both as regards rapidity of action, sharpness of image, depth of focus from before backwards, and freedom from distortion. Those of a larger size are not only very much more expensive, but are more liable to vary in quality; and it often happens that the operator fails in getting a really serviceable instrument, even after having paid the full price.

The No. 1 Portrait Lens, of 1$\frac{3}{4}$ inch diameter, 4$\frac{1}{2}$ inches focus, will take pictures on plates 4 × 3. The No. 2, of 2$\frac{1}{2}$ inches aperture, may cover a plate of 5 × 4, and produce a portrait of a size for mounting in a scrap-book. No. 3, having an aperture of 3$\frac{1}{4}$ inches, is the one commonly used for plates 6$\frac{1}{2}$ × 4$\frac{3}{4}$.

Lenses are constructed for taking both portraits and views; the back combination being removed, and the front glass turned round and inserted in its place when the Lens is employed for the latter purpose. Such arrangements have of late been much improved, and when economy is an object, the amateur will find it worth his while to make trial of an instrument of this kind.

In taking *groups*, Lenses of rather long focus are the best, since they admit of being placed at a greater distance from the object, and therefore give more depth of focus. Lenses of the same diameter may usually be bought of two different focal lengths. Arrange the group pyramidally, the tallest towards the centre, and stop down the Lens until everything is rendered equally sharp. The mode of making pasteboard diaphragms is described in the next Section.

In cleaning the glasses of a Lens which will sometimes be necessary before taking a picture, use wash-leather, as being less likely to scratch the glass than silk; and observe that the back combination of a portrait Lens consists of two distinct glasses, but in the front combination, the flint and crown are cemented together, and cannot be separated (p. 78).

DIRECT POSITIVES ON GLASS.

The remarks on the arrangement of apparatus which have been made in the preceding pages refer both to Positives and Negatives, but in the few remaining observations the two processes must be considered separately.

In the First Division of this Work (p. 141), the theory of Collodion Positives has been explained, and in the Chapter immediately preceding the present, formulæ for the Collodion, Bath, and developers, are given at length. The first Section of this Chapter describes those manipulations which are common both to Positives and Negatives, but omits such details of development, etc., as are peculiar to the former.

In developing a glass Positive, the solution of Sulphate of Iron should be scattered evenly over the film, and in some quantity, so as to wash off a portion of Nitrate of Silver into the sink. In the case of Negatives it is an object to save every trace of Nitrate, and precipitate it upon the image, in order to increase the density; but with Positives there is a fear of getting an excess of intensity, and if the Collodion film be tolerably creamy, it will always retain more than enough of the Nitrate to give a Positive free from the green or blue marks characteristic of deficient reduction. White stains at the margins of the plate are produced in great measure by the developer coming into contact with an excess of Silver.

Tilt the developing fluid backwards and forwards upon the film for about thirty seconds, or a minute, until the darkest shadows *begin* to be visible. Supposing the film to be well lighted with yellow light, there will be no difficulty whatever in ascertaining when the image is fully out: the developer must then be poured off immediately, and the plate washed with water, or the image will be rendered too dense by fresh precipitation of Silver (p. 40), and the middle tints in the face will be lost in consequence. The blacks are rarely quite pure when the plate has been too much developed, but show either little spangles of Silver, or a general clouding.

When the Sulphate of Iron is washed off before the proper development is complete, the whole image looks very thin and weak, with a blue or greenish tint: the details in the shadows may perhaps be visible, if the plate was fully exposed, but usually they are more or less defective. The difficulty with the beginner is to distinguish the effects produced by wrong exposure in the Camera, from others due to faulty development. A little care, however, will usually enable him to do so. If no details appear in the dark shadows, the image is either under-exposed or under-developed, but in the latter case the lights would be very poor and thin, as before described; whereas in the former they would probably be vigorous, especially if the operator kept the Sulphate of Iron for a long time upon the film with a hope of bringing out the shadows.

The finished picture in another case, the reverse of the last, may appear altogether too white and flat, without any deep shadows, every portion of the plate showing more or less of a deposit of Silver. In this instance it is either over-exposed or over-developed, but probably the former, and particularly so if the lights are not of a very good colour, but appear grey and feeble, *and if the whole image shows very fairly as a Negative when held against the light.* You may always calculate upon diminishing excessive density of the face and light parts by over-exposing in the Camera (p. 39), but over-development makes them quite opaque, so that the black varnish when placed beneath does not show through. On the other hand, a prolonged exposure produces a far greater effect in clouding over the shadows, and giving a grey colour to black drapery, than any amount of over-development.

When all the Chemicals are in good working order, the finest Positives are obtained by giving a rather short exposure in the Camera, because the lights are then of a pure white, and the shadows transparent. With a Collodion not suitable for Positives, the image would be too intense when developed after a short exposure.

Wash the plate with Water, to remove the whole of the Iron, before putting on the Cyanide, or a blue deposit will often be formed. The Cyanide is used over and over again until exhausted.

In mounting glass Positives it has become a common practice to cover the back of the glass with black varnish, and to mount the picture with the Collodion side unvarnished and towards the eye. The image is necessarily reversed, but the whites are very bright, and the shadows sufficiently clear if the Collodion be of the transparent kind. The only question is whether such a plan can be considered a safe one as regards *permanency*, since it has been ascertained that unvarnished films of Collodion will occasionally decompose from the edges to the centre, unless carefully washed and well protected from moisture (p. 209).

NEGATIVE PORTRAITURE.

In the Seventh Chapter of Part I., the general mode of producing Negatives has been explained: and the formulæ for solutions and details of manipulation, with the necessary apparatus and mode of arrangement of sitter, have been described at pages 284, 290, and 309 of Part II. It remains only therefore to give advice on the proper state of the Chemicals.

Collodion.—The circumstances under which Negative portraits are taken, vary so much that no uniformly applicable directions can be given. The requirements of the professional Artist, working all the year round, and often in a badly-lighted studio, are quite different from those of the Amateur who takes an occasional portrait in the open air, and usually at the most favourable seasons of the year. Advice suitable for one would not be so for the other, and hence we consider the two cases separately.

To commence with the former, we observe that the normal Collodion of page 262, iodized with the Potassium salt, has been much used for portraits in the studio. Some have spoken of it as being highly sensitive, but somewhat wanting in contrast and intensity; others, as possessing full intensity, but lacking extreme sensitiveness. One cause of the discrepancy may perhaps be that a Collodion of this kind iodized with Iodide of Potassium, is apt to vary slightly with the length of time it has been kept in the plain state, and with the purity of the Ether, which unfortunately cannot be controlled. The Artist is therefore recommended to take a trial picture, and to vary the mode of development according to the effect obtained. When the Collodion colours very slowly after iodizing, it will be likely, *cæteris paribus*, to yield a soft Negative, and if so, Pyrogallic Acid will be indicated. A rapid liberation of Iodine, on the other hand, will show that some decomposition has taken place, and if so Sulphate of Iron will probably be required to keep down the intensity of the Negative.

Observe in using this Collodion that it sets rather rapidly upon the glass, and therefore in a small and heated room no time must be lost in dipping, or the Iodide of Silver will be thrown down *upon* the film, instead of *in* the film, and both intensity and sensitiveness will be lessened. Also notice that the Collodion has a tendency to give fine black lines in the direction of the dip of the plate, which must be remedied as advised at page 300.

The Author has been requested to give in this Edition of the Work a formula for a portrait Cadmium Collodion, since many operators desirous of obtaining a constant sensitiveness prefer it to that iodized with the Potassium Salt. The normal Collodion of page 262 admits of being iodized with Iodide of Cadmium, and some have considered it highly suitable for that purpose. It always appeared however to the Writer himself that this Collodion, being intended for a Potassium iodizer, must of necessity *set* rather too rapidly upon the glass when iodized with Cadmium, and must also become surface-dry too speedily. The indication was therefore to produce a Pyroxyline of a somewhat less horny character, and one of which the film would remain moist sufficiently long to invite the progress of the developer instead of repelling it. It was also equally important to hit the exact point as regards contrast, because if this quality is in excess, the portrait will be wanting in harmony and gradation; and it must be borne in mind that in the case of a Cadmium Collodion the operator loses that control over the intensity which he ordinarily gains by keeping the Collodion after iodizing. Another point was that the half-tint of the background should be perfectly even, and free from mottling or hair-like lines. How far success has been obtained in each of the above particulars the operator himself will decide when he has prepared the Collodion by the accompanying formula,* and given it an extended trial.

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* *Formula for a Portrait Cadmium Collodion.*—In the following directions, the reader is supposed to have studied the theory of the manufacture of Collodion in Part I. and also its practical details in the First Chapter of Part II. Take of

Oil of Vitriol, sp. gr. 1·845	2 fluid ounces.
Pure Nitric Acid 1·45	1 fluid ounce.
Water	5 fluid drachms.
American Cotton	40 grains.

The Nitric Acid should be colourless and free from Chlorine, the Cotton purified by dilute Potash and dried. Time of immersion in the acids, ten minutes. Temperature 150° Fahr.

The rule for bringing the acid mixture to the proper strength is to continue the addition of Water until the Pyroxyline is only partially soluble in Alcoholized Ether, and leaves a whitish sediment in the Collodion. It would not be safe to continue the addition of water until the acids dissolved a considerable portion of the Pyroxyline, since in this formula the tendency to solution in the acids is not so great as when the proportions of Sulphuric Acid and Nitric Acid are as 3 to 1 instead of 2 to 1: hence acids weak enough to dissolve thirty per cent. of the product, would yield a Pyroxyline leaving too much sediment in the Collodion. The Pyroxyline ought to be decidedly disintegrated in appearance, but less so than that for the Normal Collodion of page 262; if 40 grains of cotton are put in, 50 grains of Pyroxyline should be taken out.

It will be far easier to work with the acids stronger than here indicated, but the Writer does not advise it, because he finds that when the Pyroxyline leaves the acids in a tough and unbroken condition, the quality of the resulting Collodion as regards fluidity and perfect smoothness of the portrait background, is injured. You have, it is true, a more marked intensity of image

The Writer's own opinion as regards the excellencies and defects of this Collodion is as follows:—It does not produce an intense image, but rather the contrary, and hence certain precautions must be taken. In the first place the operator must obtain the best quality of Nitrate of Silver; since the slightest trace of the impurity mentioned at p. 135 would produce indistinctness of image and blurring or halation. In a rather dull light, *a trace* of Acetate in the Bath will be an improvement, and in any case the solution should be nearly neutral, since excess of Acetic Acid lowers the intensity. Saturate the Bath as fully as possible with Iodide of Silver, or there may be defects, in the shape of transparent markings. The state of the developer must also be attended to when this Cadmium Collodion gives too little intensity; the proportion of Pyrogallic Acid may be increased to 1½ grains, and that of the Acetic Acid diminished to 10 minims. Half a drachm of spirit may also be required to make the developer flow, since on account of the great strength of the Alcohol in the Collodion, there is still some tendency to repel liquids, when the Nitrate Bath is newly prepared, and nearly free from Alcohol.

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and less liability to spots, but this is more than counter-balanced by a woolliness of the background, and a glutinous state of the Collodion as it nears the bottom of the bottle. On the other hand, it must not be attempted to use the acids weaker than here indicated, because in that case the loss of Collodion from sediment would be considerable, and not only so, but the image would be deficient in intensity, and would exhibit a blurring of the lines, or "halation," due to irregular deposit of Silver in the development.

To prepare the Collodion, take of

Ether of ·725	4 fluid drachms.
Alcohol of ·805	4 fluid drachms.
Iodide of Cadmium	4¼ grains.
Pyroxyline	5 grains.

The whole of the Alcohol is used in the so-called absolute state, because the Collodion, being more porous than the normal Collodion of p. 262, and setting less rapidly, is not improved, but rather the contrary, by the presence of water. The sedimentary layer of fluid in the Collodion ought not to measure more than $\frac{1}{12}$th of the total bulk. Allow to stand for a fortnight before decanting, as the fluid will then have time to clear itself, and the sensitiveness will be greater than at first.

If it be desired to impart to this Collodion the property of changing slightly by long keeping, and of giving greater intensity, about ¼th of a grain of Iodide of Magnesium may be added to each ounce.

Lastly, let a stock of the Collodion be always kept on hand, since age increases the intensity; and mix the new with the old as circumstances dictate. With a long-focus Lens the image will usually require a little strengthening by extra development, and for this purpose the solutions described at page 229 answer admirably.

The above-mentioned Cadmium Collodion, although producing a rather feeble image, is remarkable for its sensitiveness. The want of intensity may probably be one cause of its great rapidity, since organic reactions of Pyroxyline appear incompatible with excessive sensitiveness. Not only is the Negative obtained by a short exposure with this Collodion, but it is remarkable for its roundness or stereoscopic effect. As you look at it, the image seems to stand out from the glass, and to be approaching towards you. An intense or organic Collodion could not give such an effect, because the exposure required to impress the shadows would be so long that the lights would be flattened. Every ray must make a distinct and simultaneous impression upon the plate, to constitute a good portrait Collodion. If the Chemicals are in that perfect order that the Writer is now supposing, the whole of the image will develope even after an insufficient exposure: an inferior sample of Collodion gives no detail in the shadows when under-exposed, but this Cadmium Collodion will exhibit under such circumstances, an image perfect in itself, although too faint to admit of strengthening.

One word more before we leave this subject. Spots and fogging are often complained of with the Collodion now under discussion. The only remedy is great care and cleanliness, since the exquisite sensitiveness of the Collodion implies a corresponding delicacy. Specks of dust, moisture on the glass, and impurity of Chemicals, are ruinous to the working of the Collodion, and the operator, unless well armed, will be unable to succeed.

Collodion for open-air Portraits.—The normal Collodion of page 262 is not invariably successful when used with a Lens of short focus in the open air: the contrast and intensity are often too great; and when such is the case, the image will be either red and solarized, or black and white without middle tints. The sensitive Cadmium Collodion of page 320 is mostly free from this defect, but an amateur would usually find it too sensitive, and too liable to spottiness. Better than either in the majority of cases is the normal plain Collodion, *bromo-iodized* by the third formula of page 284, and developed with Sulphate of Iron. This preparation is very uniform in sensitiveness, free from all tendency to spots and fogging, and produces harmonious Negatives, very suitable for portraits. The only difficulty is in the matter of intensity, and to secure this desideratum, the Collodion should be kept for a few weeks in the iodized state, and the Nitrate Bath should be freed from Nitric Acid: the Negatives must also be rather under-exposed than over-exposed, and when the image is developed in all its details, the Sulphate of Iron must be washed off, and a mixture of Pyrogallic Acid and Nitrate of Silver employed to intensify, according to the directions given at page 306.

To give an idea of the certainty attending the employment of bromo-iodized Collodion, the Writer may mention that he has seen as many as thirty Negatives taken successively without a single failure either from dirty glasses or from markings, although the slides were passed backwards and forwards into the hands of assistants, and were repeatedly left standing for many minutes whilst the focus was being taken. This process therefore is one which will bear rough usage, and when the light is strong enough to give full intensity, it is highly useful.

Those who experience a difficulty in obtaining a proper contrast of Negative with the normal bromo-iodized Collodion, may prepare the Pyroxyline by the method described at page 342. The forehead and face of the portrait will then be abundantly opaque, but the Writer does not recommend this formula, since the sensitiveness is less, and after keeping the Collodion for a time the contrast becomes greater than is required, and more Bromide is needed to reduce it. A want of intensity and contrast in the normal bromo-iodized Collodion is, according to the Writer's experience, frequently due to the film having been partially dried up by heat, and held too long in the hand before dipping in the Bath; the Collodion being at the same time newly iodized.

SECTION III.

Landscape Photography with Wet Collodion.

The Apparatus.—As this Work is addressed principally to one about to commence the practice of Photography, let the Writer advise him not to be induced by the hope of obtaining large pictures, to purchase a photographic apparatus of a very considerable size: he will find that plates above ten inches by eight, will involve an amount of baggage which in travelling becomes a burden.

The expanding and folding Camera, made from well seasoned wood, is a useful instrument, and although many prefer to employ a rigid Camera with the Chemicals packed in the interior, yet the experience of the majority is in favour of the former. Cameras with cloth or accordion-shaped bodies are very portable, and useful when made in a proper manner so as not to crack; but the back of the Camera which carries the slide must be immovably fixed by a screw, to prevent it from shaking in a high wind. Cloth and leather contract dust and require occasional cleansing.

The Lens for plates of the size above named may be an achromatic meniscus of fifteen inches focal length, with three diaphragms mounted square, rather than in a *cone*, which is liable to give reflection from the sides. It is recommended to paint a narrow black circle of about an eighth of an inch wide at the posterior surface of the Lens, to prevent the edge of the glass from reflecting; also to put in a second diaphragm rather larger in size and made of blackened cardboard, *behind the first*, in order that a portion of the oblique rays which otherwise would strike off from the interior of the brass mounting may be intercepted. These precautions are not actually necessary, but they have been adopted by many of our most successful landscape Photographers.

A thin partition in the body of the Camera itself has also been found to improve the brilliancy of the image: it should be placed about midway between the Lens and the ground glass, and the aperture ought to be of such a size as to admit only those rays which fall directly upon the plate. A more simple plan, and one nearly as effective, is to line the interior of the Camera with black cotton velvet, taking care to place the nap of the velvet *towards* the Lens. Tripod stands should be firm and unyielding, and are recommended *not* to fold in the middle.

The merits and demerits of the Orthographic or Orthoscopic Lens of page 77 are now well understood. It is allowed to be an excellent Lens for working at close quarters on architecture, since perpendiculars tending to fall inwards are by the hour-glass distortion of the Lens thrown outwards at their extremities, and will thus appear straight. The Lens may also for the same reason be tilted a little upwards, a great advantage in practice, since the building is usually too high to be included in the field when the Camera is horizontal. Architectural subjects being nearly in one plane, are adapted to the Orthographic Lens, but with pure landscape, including foreground and distance, this Lens is unsuitable, because with the full aperture it gives an insufficient depth of focus, and when stopped down, the exposure is long and the Negative feeble. Neither is the distortion of the ordinary View Lens a very objectionable feature in a landscape, although it is fatal to the beauty of an Architectural Photograph.

The Nitrate Bath may be carried in a glass trough, with a tight top of Caoutchouc, and mounted in a wooden case for protection. Fasten a little sheet rubber round the bottom of the dipper to prevent it from cracking the trough if inadvertently dropped. Gutta-percha troughs are much used, and when the Gutta-percha is pure the Writer has not found them to injure the Bath, but they ought always to be cleansed, as described in the Appendix, Part III., since much of the commercial article is adulterated, and decomposes Nitrate of Silver.

The late Mr. Archer contrived an ingenious form of Camera, in which the operations of sensitizing and developing the plate could be carried on in the interior of the instrument. Very good pictures have been taken in this Camera, and the Author has seen it used by the inventor himself with perfect success. Nevertheless he is disposed to recommend some form of tent in preference, unless the operator be possessed of considerable tact and dexterity.

They are several tents which have been well spoken of for field work. The following, by Mr. Levi, is very simple, and may be constructed at a small expense:—*

The tent consists of:—1st. Two boards, each 30 inches in length by 15 in breadth, and $\frac{5}{16}$ of an inch thickness, hinged together by strong hinges. Each of these boards is formed of a frame of hard wood, such as nutwood, to give it strength, with a panel of deal for lightness. In the outer corners of each are holes 1 inch in diameter, a small iron plate with a corresponding opening being screwed over each hole. Each of these plates is 2 inches square.

2ndly. Four poles of light strong wood $\frac{15}{16}$ of an inch in diameter. Each pole is formed of two parts fitted together by a brass friction tube fixed on the top part of the pole. The bottom part, 41 inches in length, has an iron point at the end (fixed on by a ring), to plant in the ground if necessary; the top part, 35 inches long, has a small iron point at the end, 1 inch long and ¼ inch diameter. The two poles fitted together have an entire length of 6 feet 1½ inch.

3rdly. The covering of the tent, formed of two thicknesses of ordinary calico, dyed yellow, and sewn in such a manner that the seams do not correspond. This covering has the form of a cube, open on one side, that side continuing in the shape of a sack, with a cord passing round the opening, so as to be able to tighten it round the waist of the operator. In the bottom part of this cube are four openings, fitting exactly the poles, and corresponding to the openings in the table; these holes are bound with leather. On the opposite face of the cube are four smaller holes, equally trimmed with leather, and fitting exactly on the four small pins on the poles.

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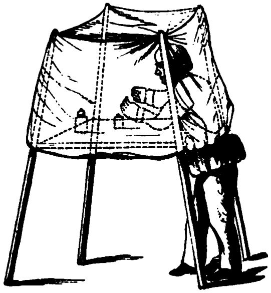
* 'London Photographic Journal,' vol. iv. p. 43.

The tent is packed by putting the eight half-poles on the closed table, surrounding them by the covering doubled up, and strapping the whole together. To mount it, the table is inserted in the covering, and opened (with the hinges downwards) so that the holes correspond with the bottom holes in the covering; the bottom half-poles are passed through these openings, a small peg fitted on them, preventing them from passing too far, and forming a rest for the table when in place. Two persons taking hold of the corners of the board and the poles at the same time, place them in position, that is to say, stick the points in the ground—not vertically, but bringing them outwards slightly on the diagonal of the table, which thus remains horizontal and perfectly firm. The four top poles are then put inside the covering and each one fitted on the corresponding half (the two parts of each pole being numbered to correspond), the iron spike at the tops being first inserted in the corresponding hole.



It only remains to put in the photographic implements; when the plate is ready to be dipped in the Nitrate Bath, or developed, the operator puts the top part of his body through the opening, the assistant ties the cord tightly round his waist, and the arms and upper part of the body remain perfectly free, and in no ways cramped for room.

It takes three minutes to mount, or to undo the tent; its weight when strapped together is thirteen pounds, and the total cost 24*s.* 6*d.*, viz. 18*s.* for purchase of calico, dyeing, and making up the covering, 3*s.* for carpenter's work, and 3*s.* 6*d.* for smith's work.

In working with this tent, the Writer has found it advisable to add one thickness of black calico *inside* the yellow, leaving an aperture of a foot square for a window; and also to attach strong cords to the top of the poles, and peg them down to the ground.

Glass plates may be carried in a grooved-box with a brass handle affixed, and water for washing the plates, either in a gutta-percha bottle, or in a tubular vessel made of Mackintosh cloth, which is suspended by a ring to the interior of the tent, and carries a flexible tap.

Thus there will be three principal packages to be carried into the field. 1st. The Camera folded in its leathern case. 2nd. The tent. 3rd. A box of leather strengthened at the corners and lined with green baize, containing the Bath, glass plates, and chemicals. In addition to this may be mentioned the Tripod legs, and the Lens in a leather case slung across the shoulder.

The full list of apparatus and chemicals required for a few days' trip of landscape Photography, is as follows:—Camera, slide, and focussing screen, with extra greyed glass for ditto in case of fracture. Large focussing cloth with strings in front, view meter,* and focussing glass. Tripod-stand with screw bolt. Lens in case. Nitrate Bath filled with solution. Half-pint solution extra in glass bottle. Spare dipper for Bath, with piece of marine glue for cementing, if required. Carbonate of Soda, one drachm. Glass plates in box, with any number extra. Linen cloth and leather for polishing. Broad camel's-hair brush. Pneumatic plate-holder. Fifteen ounces of plain Collodion. Five ounces of iodizing solution. Five ounces of Cadmium Collodion. One ounce of iodizer containing Bromide

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* This little piece of apparatus is not essential: a very good form consists of a Ramsden's Positive eye-piece, which may be made to serve also as a focussing glass. See 'Liverpool Photographic Journal,' vol. ii. p. 249.

(p. 284). Two four-ounce stoppered bottles for iodized Collodion. Two or three spare ditto, various sizes. Bottle of Varnish. Three ounces of Ether and Alcohol, mixed. Ditto, of absolute Alcohol. Ditto, of Spirits of Wine. Two-ounce measure. Half a quire of blotting-paper. Two hand-cloths, with sponge or tow for wiping. Half an ounce of Pyrogallic Acid. Four ounces of glacial Acetic Acid. Half an ounce Citric Acid. Twelve-ounce bottle for solution of Pyrogallic Acid. Sulphate of Iron, one ounce. Six-ounce bottle for solution of ditto. Cyanide of Potassium for cleaning fingers. Two or three small developing glasses, holding each twelve drachms. A dropping-bottle filled with Nitrate Bath solution (see page 305). Hyposulphite of Soda, eight ounces. Six-ounce bottle of saturated solution of ditto. Photographic tent, with table, poles, covering, and cords for fastening to the ground. Gutta-percha tray, 12 × 10. Water bottle. Scales and weights. Minim measure. Gutta-percha funnel for filtering the Bath. A yard of yellow tammy or calico. Ditto of black calico. A ball of string. Paper of pins.

The leathern case which is actually carried into the field contains only a portion of these Chemicals, viz. two four-ounce bottles of Collodion; developing solutions; dropping-bottle and small glasses; Hyposulphite fixing liquid; Ether and Alcohol for diluting, etc.: all of which should be in turned wooden boxes.

Before starting, it will be well to ascertain that the chemicals and apparatus are in working order, and in particular, that the tent does not let in the light. Prepare a plate therefore in the tent, and rear it up on blotting-paper immediately opposite to the yellow window, for at least two minutes. It ought, after this, to stand the action of Pyrogallic Acid without any staining. This point is of importance, because it will be required sometimes to give the plates a long draining, and therefore there must be security against the presence of even a trace of white light.

Having proved the tent to be tight, next see to the Camera, whether light gets in between the two portions of the body (p. 314); if it does so, the focussing cloth must invariably be thrown over the instrument during exposure.

Collodion and Nitrate Bath for Landscapes.—The normal Collodion of page 262 may be safely recommended for landscape work on plates 10×8, and 12×10. The film has a little too much tendency to repel the developer when the Nitrate Bath is entirely aqueous, but this disappears as Alcohol accumulates in it. The Negatives are also rather too hard and intense in sunny weather, especially so when the plain Collodion has undergone partial decomposition by long keeping before iodizing, or if the sample of Ether was impure. These defects the operator may have to encounter, as also a tendency to white spots if the Collodion is very new and sensitive. Develope with Pyrogallic Acid and Acetic Acid as a rule.

It will be well to iodize a portion of the normal Collodion about three weeks or a month before use. When the colour becomes of an amber-yellow you will find that although slow in action, it is admirably adapted for distant views uniformly lighted. New Collodion would produce a thin red Negative under such circumstances, and would probably fog during development: age increases the contrast and favours clearness and brilliancy. For architectural subjects the old Collodion is also better as a rule, since it gives greater decision and sharpness to the lines.

The rapidly-acting Cadmium Collodion of page 320 is useful on occasion for glens and other views lighted from above, but it is liable to solarization and other defects alluded to at page 321 if employed too frequently alone. Mixed with the normal Collodion, it assists in bringing out the shadows when the organic reactions due to decomposition are excessive. Pyrogallic Acid and Citric Acid is a suitable developer for this Collodion in a strong light.

In many works on landscape photography Bromides are said to aid in rendering the green foliage. In this opinion the Writer does not concur, having found that simply iodized Collodion of the most sensitive kind is better for giving details in foliage. The Bromide however is useful in many ways, sometimes in keeping back the shadows when a highly sensitive iodized Collodion gives too flat a picture. At other times in remedying defects of the Pyroxyline such as excessive hardness and insensitiveness due to decomposition, or again in obviating over-action of light, and thus harmonizing the sky with the landscape beneath. The normal Collodion of page 262 bromo-iodized, has been examined by one of our most successful landscape Photographers, and is reported to answer for plates of 10 × 8, or 15 × 12, but to be deficient in contrast unless kept after iodizing, and to yield more intense Negatives in the winter than in the summer. This latter peculiarity doubtless depends upon the contraction of the film which takes place in hot weather, thus impeding penetration by the developer. Amateurs would obtain feeble landscape Negatives with this Collodion when bromo-iodized, and the formula of page 342 is recommended in preference. The Pyroxyline in the latter formula produces greater contrast, and the bromized Collodion, although slow in action, gives a good quality of Negative. Sulphate of Iron, followed by Pyrogallic Acid, as directed at page 306, is the proper developer for bromo-iodized Collodion, but in hot weather a solution of Pyrogallic Acid containing two grains to the ounce of water, with ten minims of Glacial Acetic Acid and twenty minims of Alcohol, may be substituted: it will flow more easily and be less liable to produce stains.

The Nitrate Bath is often a source of trouble to the landscape Photographer, for in travelling, the sediment is washed off from the sides of the gutta-percha trough, or if it be carried in a bottle and poured out into the trough, *spots* may appear in the first few pictures, or more rarely the development may be reversed, and a "transmitted Positive" obtained in place of a Negative. Not until very recently has the manufacture of Nitrate of Silver for Photographic purposes been thoroughly understood, so that many of the above anomalies may have been due to the employment of Nitrate of Silver containing traces of organic impurity. However this may be, the opinion is almost universal, that in travelling with a Nitrate Bath, a ready means of adding Acetate should always be at hand; and the Bath should, if possible, be carried in a vessel perfectly full.

Mr. Russel Sedgfield recommends that in taking interiors a second Nitrate Bath should be used much weaker than the first, and the plates be washed in it previous to exposure, in order to reduce the quantity of free Nitrate of Silver upon the surface and thus to lessen the ill effects which result from the drying of the film during the necessarily prolonged exposure. The second Bath may contain 15 grains of Nitrate of Silver to the ounce of Water; and the difference of sensitiveness, although very decidedly seen in operating in the ordinary way, will be less perceptible when the plates are kept fifteen to twenty minutes between sensitizing and development.

Manipulations.—The principal difficulties to be apprehended are from heat and dust. To avoid them, pitch the tent if possible in a cool and shady place, and after setting it up, wipe the table inside with a damp cloth. Coat the plate rather rapidly, and give it the full rocking motion before setting. It is very desirable to keep it in the Bath as long as possible, on account of the tendency to vinous streaks and lines, but on the other hand, when the temperature of the Bath solution is high, the chances of fogging are greatly increased by leaving it in the liquid, and the Writer has been informed by one who has had much experience in hot climates, that the only plan there practicable with a simply iodized Collodion was to dip and remove almost immediately, allowing not more than thirty or forty seconds in the Bath.

When the slide is carried to a long distance, such as five or ten minutes' walk from the developing chamber, fold the focussing cloth round it and be careful that it is not much shaken or tapped against the Camera legs.

Give rather a long exposure, since it is a common error to allow an insufficient time in the Camera: the result of which will be an intense Negative, with the foliage very dark. As an average, three minutes will be sufficient for a near view well lighted, or thirty seconds for a distant view including sky and water. Six to ten minutes may be required for an interior, or a bit of forest scenery in which the light comes from above. These remarks apply to Collodion of a straw-yellow colour, and a Lens of 15-inch focus and $\frac{3}{8}$-inch aperture.

Ought the view to be sunlit or not? A good diffused light for three-fourths of the exposure, with the sun peeping out at the latter end, is to be preferred, but with Collodion and Bath in the best order, and both free from organic decomposition, a long exposure will give everything in correct gradation, even in the brightest sunlight. In other cases the means before suggested for remedying excessive contrast and hardness of Negative must be tried (p. 168). It is said that the Camera ought to be turned *away* from the sun, lest the rays should strike upon the glass and cause irregular reflection, but as it is sometimes convenient to neglect this rule, a projecting shade may be carried out in front of the Camera.

In whatever position the Camera be placed, observe that it is carefully levelled, since it is only with a Petzval Lens that you can venture to point the instrument at all upwards without destroying the perpendiculars. It will be found convenient to rule the greyed glass with a number of vertical lines parallel to each other, by which the position of the marginal parts of the image may be at once seen.

Before removing the plate from the slide for development, all the solutions should be placed near at hand, the Pyrogallic Acid in a small beaker or bird-glass, and the dropping bottle containing Nitrate of Silver. Whether the plate is to be redipped in the Bath before development will depend upon the skill of the operator and upon the length of time it has been kept. The Writer has worked successfully in cool weather with films which have been out of the Nitrate Bath for twenty minutes; a full sweep was required to carry the developer up to the edge, but when once started, the action proceeded with regularity. The plan of redipping is always attended with a danger of fogging, but it may be used with some samples of Collodion which give unusually clear pictures. Remove at once after the second dip, and drain away most of the excess of Nitrate with blotting-paper, otherwise the developer will not amalgamate with the film. It is not uncommon to find the Negatives very grey and metallic on plates which have been carried a long way after sensitizing, but this generally indicates that the Collodion is made from decomposed Pyroxyline, or that the Bath is out of order (p. 135). A second dip in the Bath will not be likely to remedy this defect.

The Writer has been desired to give a formula for a concentrated solution of Pyrogallic Acid, to be simply diluted with water when used, thus avoiding the necessity of carrying scales and weights. This plan has indeed been followed successfully; forty grains of Pyrogallic Acid being dissolved in one ounce of Glacial Acetic Acid, and twenty minims added to an ounce of water when required for use. The strong solution becomes black from decomposition in the course of a few weeks, but when diluted it has only a faint yellow tint, and is tolerably effective in bringing out the image. In place of Acetic Acid strong Alcohol may be used as the solvent, half a drachm of Pyrogallic Acid being dissolved in one ounce of spirit, and twenty minims of the resulting liquid added to each ounce of acidified water. No attempt must be made however to combine Acetic Acid and spirit in one solution, since abundance of *Acetic Ether* would be generated by so doing. These plans of preparing a concentrated developer are useful for a few weeks' keeping, but are not recommended for an unlimited time.

Having applied the Pyrogallic Acid to the film, keep it waving backwards and forwards and observe its behaviour. If it turns muddy and the image comes out rapidly, this may be due to the great heat of the tent, and it can scarcely be hoped that the picture will be free from stains after fixing. Proceed then to bridle the reduction by use of a stronger Acid, as advised at page 164.

Sulphate of Iron has been mentioned in the first part of this Work as an occasional substitute for Pyrogallic Acid, when from a want of intensity in the light, or some other cause, it is difficult to bring out the dark parts of the picture; but an objection to its use in Landscape Photography, with simply iodized Collodion, is the danger of *staining* the Negative. This is particularly liable to happen when the plates are exposed for a lengthened time, as in copying interiors, etc., and then carried to a considerable distance before being developed.

In out-of-door Photography it is often an object to economize water as far as possible, and hence the inquiries as to the minimum which will suffice for washing the plates. By some the plan is followed of letting the plate dry after development, and fixing it at the journey's end, but this cannot be recommended with all samples of Collodion. It is not uncommon in such a case to find that when the film is wetted for the second time and the Hyposulphite applied, it splits across in various parts and detaches itself from the glass. Others again have recommended a mixture of honey and water to be poured over the plate, so as to preserve it in a moist state, but the Writer has not given this plan a trial. Something will depend upon the kind of box employed for stowing the Negatives after development, for with plate boxes made purposely by the late Mr. Archer, and in which the glasses were laid horizontally, the interval of separation was so small that there was little or no evaporation, and the pictures could be fixed in the evening with impunity.

A Photographer of experience recommends that when plates are fixed on the return from the journey, a camel's-hair brush should be dipped in spirit-varnish, and passed round the edge of the film, to about an eighth of an inch inwards: the solution of Hyposulphite may then be applied without much fear of detaching the Collodion from the glass.

When the plates are fixed upon the spot, the operation should be performed outside the tent, but not in the direct rays of the sun, and the Negative must be first washed with water to remove the Pyrogallic Acid, or it will become brown and foggy on being brought out to the light. Here we experience the advantage of a capacious, flexible Mackintosh bottle, which may be filled with water and carried to a distance slung over the shoulder, thus affording abundance of fluid for removing the whole of the Hyposulphite before rearing up the Negative in the sun to dry.

This division of the chapter would not be complete without some remarks on the substitutes for distilled water when it cannot be obtained, but as this subject is fully discussed in the Vocabulary, Part III., the reader may there seek the required information.

SECTION IV.

How to Copy Engravings, Oil Paintings, etc.

In this branch of Photography we have to consider in the first place whether the copy is required to be of a reduced size, or of the same dimensions as the original, because in the latter case the operator works with a less amount of light, and hence the mode of proceeding must be different. The colour of the object should also be taken into account, inasmuch as the yellow faded tint of old prints and manuscripts is very detrimental to Photographic action.

To Photograph a full-sized steel engraving on a plate not larger than 7×6 or 5×4, is a very simple operation, and no special directions will be needed. Remove the engraving from its frame (the glass would cause irregular reflection) and suspend it vertically and in a reversed position, in a good diffused light, placing a black cloth behind it, if any bright reflecting surface be presented to the Lens. Point at it a Camera mounted with a portrait Lens, and if the image upon the ground glass appears misty towards the edge, make a diaphragm,* and place it in front of the anterior glass. Fasten on, also, a projecting funnel as decribed at page 312.

Instead of a portrait Lens an ordinary view Lens may be used, and as the field to be covered is small, a comparatively large diaphragm will suffice.

The exact state of the Collodion and Nitrate Bath is not very material; but a yellow sample of Collodion, kept a few days after iodizing, may be preferred. Be careful not to over-expose the plate, develope with Pyrogallic Acid, and fix with Hyposulphite.

The copying of old prints, manuscripts, maps, and diagrams, on plates of 10×12, 15×12, 20×17, etc., is an operation requiring greater care, and the different steps may be described successively:—

Arrangement of the Apparatus.—The Author has been at some pains in collecting information on Lenses for copying purposes. The subject is beset with difficulties, because qualities are required which appear to be incompatible with each other. The best authorities however are agreed as follows:—The old form of view Lens (p. 76) possesses certain advantages. The number of glasses and of reflecting surfaces is small, so that the light is not much intercepted in passing through the Lens; hence the image is bright, and an intense Negative is more easily obtained: in addition to this the construction of the Lens is simple, so that the optician has less difficulty in mastering it. But, on the other hand, the distortion of the common view Lens is a great defect, for it is more decided than that of any other form, and especially so if the Lens be at all strained by bringing it very near to the object. The best mode of obviating this is to employ a Lens of a tolerably long focus, and not to work it at the extreme limit. Thus if the instrument be of 20 inches focal length, and be constructed to cover a plate of 15 inches by 12, it may be used for copies of the full size up to 10 inches by 8. Beyond that, the copy, although sufficiently correct for many purposes, would not be likely to bear accurate measurement. Nothing will be gained as regards distortion by diminishing the size of the diaphragm, and the plan of pushing the stop nearer to the glass, although rendering the lines straighter, cannot often be adopted, because it makes the field concave, and thus destroys the definition at the edges. The difficulty of covering a large field perfectly flat is indeed severely felt with the common view Lens; so much so that the operator, after reducing the size of the stop as far as practicable, is often compelled to remove it to a greater distance from the Lens, even although the distortion be thereby increased.

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* Take a piece of ordinary cardboard, and cut two circles, the one within the other. The larger should be of the same size as the Lens, and the smaller that of the aperture required. Black the diaphragm with Indian Ink on both sides.

The portrait Lens of the ordinary form is remarkably well adapted for giving straight lines, and has also the merit of producing great sharpness with a large aperture. The objection is that the image is so concave as to be out of focus at the edges. Some of the best Photographic copies of maps yet exhibited were taken with a portrait Lens of 12 inches focus, stopped down by a central diaphragm of 2 inches aperture. These maps were copied piecemeal, and the separate pieces afterwards placed in junction. The portrait Lens, however, would be greatly improved for copying purposes if some mode of flattening the field were adopted so as to give better definition at the edges. Mr. Sutton, of Jersey, proposes the use of a concave Lens somewhat similar to the dispersing Lens of the Orthographic combination, and the opticians are preparing to carry out the idea. The immediate effect of employing such a central Negative Lens would be to lengthen the focus of the oblique pencils, and thus to secure a larger available field. The loss of light by reflection from the additional surfaces constitutes an objection, which must be met by cementing the Lenses when possible.

The Orthographic or Orthoscopic Lens is unequalled as regards its powers of producing a flat image on a large plate, and of throwing the light well up into the corners of the picture. The distortion, however, is greater than with the portrait Lens, although somewhat less than that produced by the old form of view Lens. In sharpness of definition it is not equal to the portrait Lens, unless a small stop be used, and the Negatives are then less easily intensified than when taken by the view Lens, since there are more reflecting surfaces to weaken the light. Many have complained of the Orthoscopic or Orthographic Lenses as being uncertain in their construction, and as often produce misty images from a false glare of light. The best instrument of the kind which the Writer has seen had a principal focus of 4 feet, and when stopped down to an inch and a quarter, would cover from 18 to 20 inches square, sufficiently sharp, and with a distortion quite inappreciable to the eye. The amount of light absorbed or reflected by this Lens was considerable, but intense Negatives could be obtained by working in the open air.

The Camera.—In a copying Camera everything should be sacrificed to rigidity, since the least vibration would produce a blurring of the lines of the picture. For ordinary purposes it will be sufficient to lengthen out a Camera of the common sort by a light cone, made to slide on at the front; but for copying maps and plans on a large scale a more substantial instrument should be provided, and should be placed upon a strong and heavy table standing on four legs. If the instrument is to stand in the open air, it may be covered in and protected from wind and rain by a movable "Punch and Judy box," with curtains at the front, sliding vertically and laterally, so as to shield the Lens from diffused light; an additional curtain being placed at the back to facilitate the darkening of the chamber around the Camera, that the operator may see the image upon the greyed glass. The importance of fixing the Camera very firmly cannot be over-rated, and the difficulty of effecting this in a satisfactory manner with a large Camera, is considerable. This you will see if you make a pencil-mark upon the greyed glass, and focus a fine line upon it: keeping the head quite still, the line will be found to vibrate from side to side, unless unusual precautions have been taken.

A flange should be fitted to the cone in front of the Camera, of a size to take the largest Lens which it is proposed to use, and for each smaller Lens an adapter screwing into the flange. Sometimes Cameras are made with the Lens working back into the body of the instrument by a perpetual screw; but this plan, although excellent as regards protecting the Lens from diffused light, has the disadvantage of throwing the front of the Camera so near to the object, that sometimes after the focussing is complete, the light is prevented from falling properly upon the lower part of the picture.

Supposing it be desired to copy the picture of the full size, fasten it to a black board, and bring the Camera up to it, until the distance equals twice the focal length of the Lens. Now, with a piece of string measure the length from the centre of the front part of the Lens to each corner of the picture; if the four measurements accurately correspond, the print is properly placed, in the middle. Next focus carefully upon the ground glass, and with a foot rule or a string ascertain that the image is of the right size, *and also that it is perfectly rectangular.* To do this compare the marginal lines with the edges of the greyed focussing glass, when the eye will at once detect any error. The picture will not be rectangular unless the Camera be absolutely level, and pointed quite at right angles to the picture; if the vertical lines, for instance, fall inwards, the front of the instrument must be a little depressed.

An inquiry is often made as to whether the sun should shine upon the picture? This question can only be answered conditionally. In the case of an old manuscript, yellow and faded, of a sepia drawing, or of other subjects of that kind, the stronger the light the better. These colours are sometimes so non-actinic that they make but little impression upon the sensitive film, and can only be copied in direct sunlight. Other prints will show the texture of the paper when copied in sunlight, and if the white parts are pure they throw off quite enough light to produce an excellent Photograph in the shade. A horizontal light is in all cases to be preferred, and vertical rays may be cut off by a narrow curtain of blue calico. The operator may also regulate the light according to the rapidity of development of his picture, which will vary with the focal length and aperture of the Lens.

It is correct in theory to increase the amount of illumination by using a portrait Lens when the image appears unusually dark upon the focussing screen, as will often be the case in copying old sepia drawings. For if a view Lens be employed, the amount of light may be too small to make any impression upon the film when the shadows of the picture are heavy: whereas, by opening up the aperture of the Lens and admitting all the rays which can be collected, a certain amount of detail will be obtained even in those parts of the picture which appear most unpromising.

The Collodion for copying.—Both the Collodion and the Nitrate Bath must be in the best possible working order, since they will be put to a severe trial in this process if the copies are to be of the full size, and if the Lens has a very considerable focal length. Collodion made from weak Negative Pyroxyline (p. 155) will not answer the purpose, the image developing in the grey metallic form, and being difficult to strengthen. No amount of keeping after iodizing will bring it into the proper state; and when it becomes much coloured from free Iodine, the amount of Nitric Acid liberated in the Bath will tend further to weaken the image and produce stains in developing.

The formula for a normal Collodion given at page 262, has been much used in copying, and this preparation undoubtedly possesses the merits of being very limpid and adherent to the glass. The Writer however finds it to be somewhat deficient as regards the required intensity, and likewise to be too sensitive for copying black and white objects without middle tints. Excess of sensitiveness is an objection in copying maps: it is difficult to preserve the transparency of lines and dots in such a case, seeing that even black surfaces throw off a small amount of light, and a very sensitive Collodion is affected thereby. Hence it becomes convenient to prepare a second Collodion with more contrast and clearness of developing than the last, and to mix them together or use them separately as occasion may require.*

Collodions for copying will usually improve by keeping after iodizing, but no definite rule can be stated. The normal Collodion of page 262 may usually be kept for a month or six weeks in cool weather, or for three months if iodized with mixed Potassium and Cadmium. The Collodion described in the foot-note loses sensitiveness more rapidly on account of the high temperature employed in making the Pyroxyline.

In place of simple iodides, the Collodion of the foot-note may be iodized with Bromide and Iodide conjoined. Many operators esteemed skilful in this branch of the art, attribute their success to the use of the Bromo-iodide, and to the sharpness of outline, with freedom from fogging and spots, which it imparts. A want of intensity constitutes

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* *Formula for a Copying Collodion.*—In the directions now given the reader is presumed to be acquainted with the manufacture of Collodion as described in Part I. and also in the First Chapter of Part II. Take of

Oil of Vitriol, sp. gr. 1·845	2 fluid ounces.
Pure Nitric Acid, sp. gr. 1·45	1 fluid ounce.
Water	½ fluid ounce.
American Cotton	30 grains.

Purify and dry the Cotton in the usual way. Temperature 170° to 175° Fahr. Time of immersion five minutes.

In the above formula the proportion of diluted Oil of Vitriol is reduced in order to render the Pyroxyline less horny. The Water is also reduced in quantity with a view of adding to the intensity, and the temperature is raised twenty degrees to lessen sensitiveness and improve the flowing qualities.

The perfection of this Collodion will depend entirely upon the Pyroxyline being exactly in the proper state; it must be broken up and small in quantity on leaving the acids, and inclined to be dusty on drying; otherwise more water should be added or the time of immersion increased from five to ten minutes. In washing the Pyroxyline a final bath of very dilute Ammonia may be used, since a trace of alkali appears to assist in giving intensity.

The Ether and Alcohol are to be in the usual proportions, and the iodizer may consist of Iodide of Potassium simply, or may contain an extra grain of Iodide of Cadmium to each ounce if the film appears too opalescent.

its only defect, to overcome which the picture may be hung in a good light, and the plate be fixed with Cyanide, and subsequently treated by Davanne's Iodine method, presently to be described (p. 345). In copying maps and plans of full size by Lenses of four or six feet solar focus, the light is, according to the Author's experience, too much reduced to yield a dense Negative with any Collodion excepting the simply iodized.

The Bath Solution for Copying purposes must be prepared with *recrystallized* Nitrate of Silver, perfectly free from that impurity mentioned at page 135, which weakens the reduction, destroys the bloom, and produces spots and stains. A trace of Acetate of Silver will be favourable rather than otherwise; about as much as would be produced by dropping a single drop of Ammonia into ten ounces of the solution, and supersaturating with Acetic Acid. The trough for holding the solution being of considerable size must be made of gutta-percha, which can be done with impunity if the gutta-percha is of good quality (p. 135). The Bath will improve by moderate use if all the chemicals are pure; the film becoming less repellent to the developer, giving rather more intensity, and yielding cleaner Negatives.

Exposure of the Plates.—No special directions will be needed under this head, excepting when the object to be copied presents merely a black and white surface. In such a case the ordinary rules for exposure fail, the middle tints being absent. When a photographic copy of a map or diagram has received an insufficient amount of exposure in the Camera, the parts of the Negative corresponding to the black lines remain very clear, without showing any disposition to fog under the action of the developer, but the lights develope slowly, and are not sufficiently intense. Slightly over-exposed Negatives, on the other hand, develope more quickly, and with a deeper shade of colour, but it is difficult to prevent the solution of Pyrogallic Acid from clouding over the lines, and thus rendering the design invisible by reflected light.

The time of exposure in copying pictures will vary much with the focal length of the Lens and the sensitiveness of the Collodion; but in the case of an Orthoscopic Lens, stopped down, as much as five minutes may be given for an oil painting, even in the direct rays of the sun. A black and white object would require about a minute or a minute and a half under similar circumstances.

Development.—This is often a tedious operation, and when the Negatives are taken in a weak light, from five to ten minutes are commonly spent in getting up the intensity to the proper point. Pyrogallic Acid will be found the best developer as a rule, when the Collodion contains Iodide only; and it will be often advisable to reduce the quantity of retarding Acetic Acid to one-half, otherwise the Silver will be thrown down in a too crystalline and metallic form. If the diminution in the amount of Acetic Acid makes the developer flow with difficulty, remedy it by adding twenty minims of Alcohol to the ounce.

In the case of engravings, paintings, sepia drawings, etc., a careful process of pushing the development in the ordinary way (p. 305) will usually suffice to give intensity, if the Collodion be in the proper state. Hold the Negative for an instant against the yellow light whilst the image is commencing to develope: if the slightest tone of *red* prevails, the continuation of the process will be easy, but when the picture is blue and silvery there will be a difficulty.

Negatives of maps, plans, printed matter, etc., ought invariably to be *under-developed* in the first instance, so as to obviate all chance of depositing Silver on the lines. The Pyrogallic Acid must be poured off as soon as the image appears in all its parts, and the Iodide of Silver cleared away by weak Cyanide of Potassium, after which the re-development may be carried on as before described. It will occasionally happen in this process of intensifying that an opaline deposit of Silver will be thrown down in a very regular manner upon the clear parts of the Negative, stopping abruptly at the points where the true image commences. When this happens, a stronger acid may be used in the intensifying developer, viz. Citric Acid instead of Acetic Acid, and the Writer has found the solutions described under the head of "Russell's Tannin Dry Process" to answer admirably for that purpose.

Artificial Modes of strengthening Negatives.—These will be required in all cases where the actinic intensity of the light falls below a certain point. In making a full-sized Negative of a Collodion Positive on glass, by means of a Portrait Lens stopped down in the way described at page 337, the method of Davanne will often be found sufficient. Throw a crystal of Iodine into Spirits of Wine until the liquid becomes very dark and opaque, then add a few drops of the solution to distilled water, enough to render the water of an amber-yellow. Too much Iodine causes a blackish turbidity in the water, but this is instantly removed by a little Spirit. After fixing and washing the picture, pour on the aqueous Iodine solution for about a minute, then wash under a tap, and expose for an instant to diffused daylight. Carry the plate back again into the dark room, and intensify with mixed Pyrogallic Acid and Nitrate of Silver in the usual way (p. 305): no second fixing will be needed.

The additional deposit obtained as above described will often be found sufficient, and when such is the case the method is to be preferred, because the half-tones of a Photograph are easily obliterated by too much intensifying. In the case of large copies of maps taken with Orthoscopic Lenses of long focus, the Iodine method proves insufficient, and the fine lines of the drawing become partly obliterated during the prolonged development. In such a case it is advised to develope the plate only partially in the first instance, and to fix it with Cyanide of Potassium; then to intensify twice with Pyrogallic Acid, Citric Acid, and Nitrate of Silver, and lastly to treat the plate with the two following liquids:—

No. 1.	Iodine	6 grains.
	Iodide Potassium	12 grains.
	Water	6 ounces.

No. 2.	Sulphide Potassium	1 drachm.
	Water	6 ounces.

Apply No. 1 either in the yellow room or in the daylight, until the whole of the image is converted into Iodide of Silver and the deposit appears yellow throughout. Then pour water on the image from a jug, and apply No. 2, which must be allowed to remain until the yellow colour changes to a deep reddish-brown. Lastly, dry the plate, and varnish in the usual way. The theory of this process is explained at page 170.

If the opacity of the Negative is not complete after the above treatment, it will indicate that the amount of real Silver in the image was insufficient to produce opacity when converted into Sulphide. A second Negative must therefore be taken, and the intensifying with Pyrogallic Acid, Citric Acid, and Nitrate of Silver continued for a longer time. Even if this continuation of the development should not appear to add much to the density, it must still be persevered with, since after the application of the Sulphide of Potassium the difference will be manifest.

SECTION V.

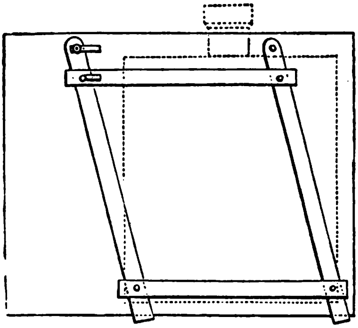
Rules for taking Stereoscopic and Instantaneous Photographs.

Binocular pictures of a large size, for the reflecting Stereoscope, may be taken with an ordinary View Lens of about 15 inches focus. The ground glass of the Camera having been ruled with lines in the manner described at page 333, the position of some prominent part is marked upon one of the lines with a pencil, and the first view is taken. The stand is then moved laterally to the proper distance, and the Camera adjusted to its second position by shifting it until the marked object occupies the same place as before. The distance between the two positions should be about one foot when the foreground of the picture is twenty-five feet from the instrument, or four feet when it is at thirty or forty yards. But, as before shown at page 93, this rule is not to be followed implicitly, much depending upon the character of the picture and the effect desired.

Photographs for the refracting Stereoscope are taken with small Lenses of about 4½ inches focus. For portraits, a Camera may advantageously be fitted with two double-combination Lenses, of 1¾ inches diameter, exactly equal in focal length and in rapidity of action. The caps are removed simultaneously, and the pictures impressed at the same instant. The centres of the Lenses may be separated by three inches when the Camera is placed at about six or eight feet from the sitter.

Pictures taken with a binocular Camera of this kind, require to be mounted in a reversed position to that which they occupy on the glass, or a *pseudoscopic* effect will be produced. The Negatives may be cut in half, the right half being printed on the left side, or the finished prints may be reversed before mounting.

Mr. Latimer Clark has devised an arrangement for taking stereoscopic pictures with a single Camera, which is



exceedingly ingenious. Its most important feature is a contrivance for rapidly moving the Camera in a lateral direction without disturbing the position of the image upon the ground glass. This will be understood by a reference to the woodcut on page 347.

"A strongly-framed Camera-stand carries a flat table about 20 inches wide by 16, furnished with the usual adjustments. Upon this are laid two flat bars of wood in the direction of the object, and parallel, and about the width of the Camera asunder. They are 18 inches in length; their front ends carry stout pins, which descend into the table and form centres upon which they turn. Their opposite ends also carry similar pins, but these are directed upwards, and fit into two corresponding holes in the tailboard of the Camera.

"Now when the Camera is placed upon these pins, and moved to and fro laterally, the whole system exactly resembles the common parallel ruler. The two bars form the guides, and the Camera, although capable of free lateral motion, always maintains a parallel position. In this condition of things it is only suited to take stereoscopic pictures of an object at an infinite distance; but to make it move in an arc, *converging* on an object at any nearer distance, it is only necessary to make the two guide-bars approximate at their nearer end so as to converge slightly towards the object; and by a few trials some degree of convergence will be readily found at which the image will remain as it were *fixed* on the focussing glass while the Camera is moved to and fro. To admit of this adjustment, one of the pins descends through a slot in the table, and carries a clamping-screw, by means of which it is readily fixed in any required position.

"In order however to render the motion of the Camera smoother, it is advisable not to place it directly upon the two guides, but to interpose two thin slips of wood, lying across them at right angles, beneath the front and back of the Camera respectively (and which may be fixed to the Camera if preferred), and to dust the surfaces with powdered soap-stone or French chalk."

In addition to this arrangement for moving the Camera laterally, the *slide* for holding the sensitive plates must be modified from the common form. It is oblong in shape, and being about ten or eleven inches long, requires some little adaptation to fit it to the end of an ordinary Camera. The glasses are cut to about 6¾ inches by 3¼; and when coated with Iodide of Silver, the two images are impressed side by side, the plate being shifted laterally about 2½ inches, at the same time and in the same direction as the Camera itself.

The operation of taking a portrait is thus performed. The focus having been adjusted, and the bars approximated about a quarter of an inch in front to give the right convergence, the Camera and the slide are *both* drawn to the left hand. The door is then raised and the plate exposed. Next, the Camera, and after it the slide, is shifted to the right hand, and the plate in its new position having been again exposed, the door is closed and the operation completed.

Pictures taken with this instrument do not require to be reversed in mounting, the left picture being purposely formed on the right-hand side of the glass.

In choosing between the Latimer Clark Camera and the Camera with twin Lenses, the operator will be guided by circumstances. If he wishes to take pictures nearly instantaneous, two separate Lenses will be a *sine quâ non*, but the effect in the Stereoscope is not so decided, and to the eyes of many, the relief of rather distant objects will be imperceptible. The Writer does not attempt to settle this vexed question, but he is informed by vendors of Stereoscopic slides, that as a rule, preference is given to those taken at a wide angle.

Instruments are now constructed which may be used either for one or two Lenses, and with any amount of separation, from three inches to a foot. Contrivances have likewise been introduced, for taking two or even three sets of pictures at one operation: a glass plate of large size being employed and the double images impressed one above the other, either by raising and depressing two Lenses placed side by side, or by shifting laterally three

Lenses arranged on a line vertical with the front of the Camera.

Portrait Lenses of the quarter-plate size are often employed for Stereoscopic Landscape Photography, instead of view Lenses, the diaphragms being placed midway between the glasses. The advantage is that one Lens may be made to answer both for portraits and views.

The Manipulations and Chemicals.—Any extended directions on this head would be superfluous. Photography on plates of the Stereoscopic size is the most simple branch of the art, and for that reason is usually recommended to beginners. The amateur may commence by reading the general theory of Positive or Negative Photography, as the case may be, in the Seventh Chapter of Part I. He may next practise the manipulations described in the First Section of this Chapter, and afterwards read such observations on Collodion portraiture and landscape Photography as he will find in the two preceding Sections. The Collodion and other chemicals are made by the formulæ given in Chapter I., Part II., and the list of apparatus and bottles is taken from page 328.

Nevertheless, to attain to first-rate excellence in Stereoscopic Photography requires skill and practice, and it is a common remark that these pictures are often defective in just balance of light and shade. The Negatives are developed too strongly, which gives to the print an appearance like chalk or snow. The brilliancy of the Camera image is in fact so great with Lenses of 4½-inch focus, that special appliances are often required to subdue the force of the development (p. 153).

It has before been shown that the intensity of development will vary much with the strength of the Nitro-Sulphuric Acid used in making the Pyroxyline. For Stereoscopic Photography in a strong light the Pyroxyline prepared in weak acids will give the softest pictures, and by using two iodizers, the one consisting of mixed Iodide of Cadmium and Potassium, and the other of Bromo-iodide (p. 284), the operator will be enabled to meet any case which may arise.

Vinous markings on the second picture, due to defective draining (p. 301), and a transparent band at the edge lowest in the slide, from a wave of Nitrate solution accumulating at the bottom, are failures common in Stereoscopic Photography. The plan of taking two sets of pictures at once upon a square plate, removes these defects in great measure, by obviating the necessity of turning the plate after draining to make it fit the slide, and by allowing a margin for stains. It is perhaps to be regretted that the ordinary Stereoscopic glass was not cut somewhat broader in the first instance, although it would be inconvenient to make any change, now that this size of 6¾ by 3¼ has been so long established.

With some samples of Collodion which have undergone organic decomposition, or with any Collodion dipped in a Bath in the state described at p. 135, only one of the two Stereoscopic pictures can be properly taken; for during the time of the impression of the first plate, the other part of the sensitive Iodide undergoes a change, and the second picture in consequence is weak and metallic. A Camera with twin Lenses must be used in such a case, or no satisfactory result will be obtained.

The state of the Nitrate Bath will require a little extra attention in Stereoscopic Photography, when the troughs are made narrow, and their capacity is small. Two or three days' hard work in hot weather will occasionally throw the Bath out of order, either from Acidity or Alkalinity, according to the state of the Collodion: and on account of accumulation of Ether, etc., the liquid will begin to run into lines as above described.

Residues of Iodized Collodion, which have lost much of their sensitiveness, may often be used up in Stereoscopic Landscape Photography when the light is good. And although as a rule old Collodion gives more intensity of image than new, yet as the density of Collodion varies much with the amount of free Iodine which causes the colour (p. 132), it sometimes happens that a bottle of Collodion previously esteemed useless, is found to produce a better quality of Negative than could be obtained with the same freshly iodized. The occasional occurrence of such a phenomenon has doubtless originated the saying that when any unusual complication of difficulties occurs in Collodion Photography, it will be well to try the plan of mixing together the contents of all the stray Collodion bottles upon the shelf.

INSTANTANEOUS PICTURES.

Pictures shown as *Instantaneous* are, as a rule, taken by a brief exposure, but yet one occupying an appreciable amount of time, as is evidenced by the fact that the outlines of moving objects are more or less indistinct. On making inquiry into the means adopted to obtain such pictures, we usually find that no precautions were taken beyond those of working with good Collodion, and admitting as much light as possible through the Lens.

Can any substance be added to Collodion which will assist it in giving instantaneous pictures? Many would answer this question in the affirmative, mentioning such bodies as Creosote, Oil of Cloves, etc., which have been said to increase the sensitiveness. But in all probability when such bodies were found to produce a good effect, the Collodion was not itself in the best possible state. It may have been made in the first instance from impure materials, or have undergone a decomposition by keeping either before or after iodizing.

With Collodion of the most sensitive kind, iodized with Cadmium only (p. 284), perfect Negative portraits have been taken in the shade (in a London afternoon light) in half a second, the Lens being 1¾ inch aperture and 4½ inches focus. The dark parts of the picture were fully brought out, a point which must always be borne in mind, since it is well known that if the artist be content to sacrifice a little detail in the shadows, he can obtain the picture in one-half of the time, and it is in the shadows that instantaneous Photographs are usually defective.

Proto-iodide of Iron has been spoken of as an accelerating agent. It will quicken old and brown Collodion considerably, but in the case of the most sensitive Collodion, a fourth or a fifth of the total exposure would be the utmost gain to be anticipated; and when we consider that Collodion prepared with Iodide of Iron soon loses its sensitiveness, and also introduces Proto-Nitrate of Iron, a developing agent, into the Bath, its use is a questionable advantage.

The Bath for instantaneous pictures should always be prepared from the best quality of Nitrate of Silver, crystallized a second or even a third time. Certain additions may be made which will increase the sensitiveness of the Bath for a time, such as a few drops of an Alcoholic solution of Gallic Acid (p. 136), or in some cases a grain or two of Glycyrrhizine. The Writer, however, hesitates to recommend them, finding that they are only suitable for certain states of Collodion, and that the effect produced upon the Bath is transitory, and ultimately injurious.

Sulphate of Iron is theoretically the proper developer (p. 167); but in this instance also the state of the Collodion must be taken into account, and with feeble Collodions employed soon after iodizing, the iron salt would be likely to produce a weak and foggy picture.

The actinic power of the Lens employed is of more importance than either Collodion or Bath, in instantaneous Photography. View Lenses of the common form are not quick enough as a rule, but good results have been obtained with Stereoscopic view Lenses corrected for spherical aberration after an improved mode (p. 73), and worked with a large aperture. Orthoscopic Lenses are slower by nearly one-half than those of the old form when stops of the same size are employed; but these Lenses ought to admit of being used without any stop, when the nature of the object is suitable, and no great depth of focus is required. Portrait Lenses stopped down to about one-half, with a diaphragm between the glasses, have hitherto been principally used for instantaneous views; and all those precautions must be taken which have before been suggested at pages

312 and 324 for the purpose of preventing diffused light from entering the Camera,—such as a funnel in front of the Lens; a black lining to the tube of the Lens; annulus of black Varnish at the posterior surface of the Lens; diaphragm in the Camera midway; and a cloth covering the Camera during exposure.

A good arrangement for a first attempt at instantaneous Photography, is a Stereoscopic Camera mounted with twin portrait Lenses. A light outside casing of mahogany, blackened in the interior, slides over the Camera when not in use, and draws out so as to project several inches beyond the Lenses when the pictures are taken; the opening of the box in front being still further contracted, if necessary, by a blackened card, with two circular apertures corresponding to the lenses. There are no caps to the Lenses, but a black cloth hangs down in front of the loose box just described, and is raised for an instant to admit the light. Begin by adjusting the two Lenses to a corresponding focus from the front, then draw out the sliding box, and (the rackwork of the Lenses being now out of reach) complete the focussing from the back. Those who desire a more elaborate arrangement than that now described may obtain it by applying to the dealers in Photographic apparatus.

In order still further to secure such an amount of success as will be encouraging, make the first trials on a clear spring morning, and at the seaside, if practicable. The few instantaneous pictures which are exhibited have doubtless been selected from a number of failures; for the operator soon finds that even with apparatus and chemicals in the best order, he depends much upon the light, and cannot always obtain the same success.

A few words of advice may be given on the preparation and development of the plates. Employ, when practicable, a commodious tent or yellow room, so as to be enabled to perform all the manipulations rapidly. You will find that if the film from *heat* or other causes becomes partially surface-dry, the Collodion will be less sensitive, and, with the same Chemicals, a considerably longer time must be allowed in the Camera. If the Pyrogallic Acid acts very quickly, and brings out a faint red image, as is often the case in using a sensitive Collodion for distant objects well lighted, *fix* the plate at once with Hyposulphite or dilute Cyanide, and then, after carefully washing with water, intensify with fresh Pyrogallic Acid and Nitrate of Silver as advised at page 305.

In conclusion the Writer desires to recommend a trial of the Bromo-iodized Collodion, of pages 262 and 284, for instantaneous pictures of animals, etc., taken in the open air. Bromo-iodized Collodion is undoubtedly less sensitive than simply iodized, but not very materially so when the Bath contains forty grains of Nitrate of Silver to the ounce of water. The great advantage is that a Lens of larger aperture may be used, and the image thrown suddenly upon the film, without giving rise to fogging during development. With simply iodized Collodion the action of the light appears to extend *laterally*, but with the Bromo-iodized the effect is more nearly limited to the parts of the Iodide which receive the image.

The Photographer may avail himself of the advantage offered by a Bromo-iodized Collodion in photographing the spots on the sun's disk. The intensity of the light is here so considerable that it is very difficult to prevent overaction when using a simply iodized Collodion; whereas the Bromo-iodide developed with a feeble reducing agent is quite manageable. One grain of Pyrogallic Acid in half a drachm of glacial Acetic Acid and an ounce of water will bring out the image rapidly; although, as already shown at page 163, such a solution is too weak for Bromo-iodized Collodion exposed in a light of only moderate intensity.

SECTION VI.

On the Photographic Delineation of Microscopic Objects.

Many specimens of Micro-photography which have been exhibited are exceedingly beautiful; and their production is not difficult to one thoroughly acquainted with the use of the Microscope and with the manipulations of the Collodion Process. It is important, however, to possess a good apparatus, and to have it properly arranged.

The object-glass of the ordinary compound Microscope is the only part actually required in Photography, but it is useful to retain the body for the sake of the adjustments, and also the mirrors used in the illumination. The eye-piece, however, which simply magnifies the image formed by the object-glass, is not actually necessary, since the same effect of enlargement may be obtained by lengthening out the dark chamber, and throwing the image further off.

Arrangement of the Apparatus.—The Microscope is placed with its body in a horizontal position, and the eye-piece being removed, a tube of paper, properly blackened in the interior, or lined with black velvet, is inserted into the instrument, to prevent irregular reflection of light from the sides.

A dark chamber of about two feet in length, having at one end an aperture for the insertion of the eye-piece end of the body, and at the other a groove for carrying the slide containing the sensitive plate, is then attached; care being taken to stop all crevices likely to admit diffused light. An ordinary Camera may be employed as the dark chamber, the Lens being removed, and the body lengthened out if required by a conical tube of gutta-percha, made to fasten into the flange of the Lens in front. The whole apparatus should be placed exactly in a straight line, that the ground glass used in focussing may fall at right angles to the axis of the Microscope.

The length of chamber which has been recommended, measuring from the object-glass, is from two to three feet, according to the size of image required : if extended beyond this, the pencil of light transmitted by the object-glass will be diffused over too large a surface, and may produce a faint picture. It will be shown, however, as we proceed, that some operators have produced good results with a Camera of double the length here mentioned. The object should be illuminated by sunlight if it can be obtained, but a bright diffused daylight will succeed with low-power glasses, and especially when Positives are taken. Employ the *concave* mirror for reflecting the light on the object in the latter case; but in the former the *plane mirror* is better, except with powers exceeding a quarter of an inch, and of large angular aperture.

The time of exposure must be varied according to the intensity of the light, the degree of magnifying power, etc. At this point a difficulty will probably occur from the plane of the chemical focus not corresponding, as a rule, with that of the visual focus. This arises from the fact that the object-glasses of Microscopes are "over-corrected" for colour, in order to compensate for a little chromatic aberration in the eye-piece. The violet rays, in consequence of the over-correction, are projected *beyond* the yellow, and hence the focus of chemical action is further from the glass that the visible image.

The allowance may be made by shifting the sensitive plate, or, what amounts to the same thing, by removing the object-glass a little *away* from the object with the fine adjustment screw; the latter is the more convenient. The exact distance must be determined by careful experiment for each glass; but it is greatest with the low powers, and decreases as they ascend.

Mr. Shadbolt gives the following as a guide:—"An inch and a half objective, of Smith and Beck's make, required to be shifted 1-50th of an inch, or two turns of *their* fine adjustment; a 2-3rds of an inch, 1-200th of an inch, or half a turn; and a 4-10ths of an inch, 1-1000th of an inch, or about two divisions of the adjustment. With the 1-4th and higher powers, the difference between the foci was so small as to be practically unimportant."

There is some reason to think that the *kind of light* employed may have an influence upon the separation of the foci. Mr. Delves found that with sunlight the difference between them was small even with the low powers, and inappreciable with the higher; whereas in using diffused daylight which had undergone a previous reflection from white clouds, it appeared considerable.

The object-glasses of the same maker, and particularly those of different makers, also vary much; so that it will be necessary to test each glass separately, and to register the allowance which is required.

Mr. Reeves Traer, who has been very successful in this branch of Photography, has kindly favoured the Author with his experience. In attempting to arrange his Microscope according to the directions above given, he failed in fixing it as steadily as he could desire, and was induced in consequence to have a brass apparatus made for uniting together the object-glass, stage, mirror, and adjustments, and screwing them bodily into the Camera. The whole then formed only one piece, and became perfectly under control.*

The Camera which he employs is about four feet in length and ten inches square. He uses a *concave* mirror of two and a half inches diameter, made purposely, the ordinary mirror having been found to be too small; and in the track of the rays of light, he places an inverted object-glass of a lower power than the one employed in magnifying, to serve as an achromatic condenser. The stage is firmly fixed in a vertical position, and has two spring clips to hold the slip of glass on which the object is mounted. There are no stage movements: but two adjustments are employed as usual, a *coarse* for focussing with low powers, and a *fine* for the higher powers. The milled head of the fine adjustment is marked into a certain number of divisions, to allow for the difference between the visual and chemical focus by a graduated rotation.

The Camera with its brass mountings affixed to it is placed upon a table in the open air, its long axis in a line with the sun's rays, so that the source of light is behind the operator as he looks into the instrument. The mirror is then shifted until the field appears equally illuminated, and the position it ought to occupy will easily be found by moving it backwards and forwards until a bright white spot of reflected light is seen on some portion of the field. When this is the case, the object-glass used in condensing is probably exactly in the focus of the mirror, which it ought not to be, and therefore the mirror must be pushed back a little, so as to allow the reflected rays to cross before entering the condenser, after which the white spot will disappear. With glasses lower than the ¼-inch a plane mirror may be used.

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* A diagram of this arrangement will be found in the fifth volume of the 'Journal of the Photographic Society.' The price charged for it by the Microscope-maker was five pounds.

The exact power of glass which ought to be employed will depend upon the nature of the object, and not so much upon the size of image required. A large image can always be obtained with a low power by prolonging the Camera and throwing the focus further off; but to exhibit the peculiar structure of some objects it is essential to employ a high power, and when low powers are substituted, surface-markings, dots, etc., are in a measure lost. In place of throwing the image further off when a large representation is desired, an eye-piece may be used, thus saving additional length of Camera. Theoretically the curvature of the field is increased by so doing, but nothing peculiar was observed in the specimens taken in this way excepting a little loss of definition. The eye-piece of *least* magnifying power is the proper one to employ, and it may be pushed into the brass tube from the interior of the Camera.

It is important to work in a bright light, and rather quickly; because if many seconds are allowed to elapse, the sun shifts its position sufficiently to disturb the circle of light formed by the mirror. Mr. Traer has not been able to confirm the observations of Mr. Delves above quoted, that the chemical foci of microscopic objectives vary with the quality of the light.

The late Mr. Howlett exhibited enlarged Micro-Photographs of a very superior quality. His experience was as follows:—It is a waste of time to work in a bad light.

The sun's rays may be condensed upon the object by means of a large plane reflector and a double convex Lens of six inches diameter. The employment of low-power glasses is most successful, and when the higher powers are used, the difficulties increase at a rapid rate. A $\frac{2}{3}$-inch object-glass is useful, the difference between the foci of which was found to be $\frac{15}{1000}$ of an inch. It is better not to use a larger angular aperture than is actually required to display the structure of the object, but to cut off the excess of aperture in some instances by a stop placed against the posterior Lens of the object-glass. The use of other Lenses added to the object-glass for the purpose of making the visual and chemical foci coincide, is not recommended.*

Chemicals and Manipulations for Micro-Photography.—The image when formed by the direct rays of the sun is remarkably brilliant, and the Negative may be obtained under favourable circumstances in one or two seconds. There are usually strong contrasts of light and shade, some parts of the image being very dark and others extremely light. The remarks therefore on Collodion and Bath made under the head of Portrait Photography will apply in this case. Intense Collodion prepared from Linen, or Cotton at high temperatures of Nitro-Sulphuric Acid, will become red in the lights before the shadows can be brought out; and if either Collodion or Bath contain organic matter such as Glycyrrhizine, Grape Sugar, etc., the evil will be increased. Acetate of Soda in the Bath is not to be recommended, for the same reason. Iodide of Potassium will form a better iodizer than Iodide of Cadmium, as giving a film less liable to solarize under a strong light. And for some objects the presence of Bromide will be an improvement; since Bromide always gives the power of exposing for a long time without producing over-action, and in a very bright light it does not interfere in getting up the intensity of the Negative.

In the case of a simply iodized Collodion, the ordinary developing solution of Acetic Acid and Pyrogallic is recommended in preference to Citric Acid and Pyrogallic Acid, the former being more adapted for bringing out the heavy shadows, which are so abundant in some Microscopic objects.

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* Photographic Notes, vol. iii. p. 168.

SECTION VII.

Photography in Hot Climates.

The Photographic Art is now so extensively practised in India and other parts of the globe, where the climate is more or less unfavourable, that the Author has been induced to devote a distinct Section to the subject. Those points which have already been explained in the First Division of the Work, or in the separate Sections of the present Chapter, will not again be brought forward, the reader being simply referred to them when necessary.

The Calotype Paper Process has until very recently almost exclusively occupied the attention of Landscape Photographers in India and other hot climates, Collodion having been found uncertain in composition and properties, and difficult to manipulate. The paper itself, however, is variable in composition, and the manufacturers do not appear to be able to produce a quality which is uniformly good for Photography. Hence there is a general disposition to employ the Collodion process, and especially so now that it is better understood.

The Calotype Paper Process, as far as the Writer can gather, is usually practised in hot climates by simply iodizing the paper and rendering it sensitive without the use of any Gallic Acid. Gallo-Nitrate of Silver has been found to decompose quickly, and to produce weak and red Negatives, with general fogging on the surface. The most common failures, in addition to the one above mentioned, are spots and woolliness, both of which are often due to the use of paper unadapted for the purpose.

On the subject of Collodion, the Author can give more exact information. The process of "baking," as a correspondent terms it, which Collodion undergoes in its transit to distant parts of India, is the reverse of favourable to a fluid containing two such unstable substances as Pyroxyline and Ether. Hence, as the above Writer continues to observe, "No two samples appear to arrive in the same condition, some being very limpid and others semi-gelatinous. Occasionally a white precipitate is seen in the plain Collodion, and when such is the case, the fluid becomes very brown on adding the iodizer, and pictures cannot be taken excepting by an exposure of almost impracticable length." These remarks were penned some years ago, and would scarcely be applicable in the present advanced state of our knowledge.

The mode of proceeding originally adopted by the Author was to send out Collodion of different qualities, and to receive reports of their general mode of working. The results were, shortly, as follows:—Collodion made from Linen is not good for transit: it becomes thin like water, and sometimes deposits a precipitate; the film is very rotten and insensitive. Collodion from Cotton at temperatures high enough to generate Nitro-Glucose (p. 115) stands better than the last: good pictures were taken with this Collodion, but it required a long exposure, and soon turned red. Collodion from Cotton Pyroxyline made at lower temperatures, and iodized with Iodide of Cadmium, succeeded perfectly.

In carrying Collodion abroad, great attention should be paid to the quality of the Ether; which in certain states is very readily *ozonized* by the Pyroxyline, and destroys the tenacity of the film. The Author finds Methylated Ether to be more changeable than pure Ether, but at the same time confesses that good reports have been received of Methylated Collodion sent out from this country iodized with Iodide of Cadmium. In this instance the Pyroxyline was doubtless of the best quality, since the Linen Collodion which decomposed on the voyage was not found to work well, even when iodized with Iodide of Cadmium.

The latter question, viz. as to the proper iodizer for Negative Collodion which is intended for exportation, is of importance, and yet a difficult one upon which to pronounce an opinion. It appears that much of the Collodion is used for portraits and moving objects, a comparatively small proportion only being employed for large views. The use of Cadmium therefore is a great security: because if the Ether becomes partially decomposed in its transit, the chance of obtaining quick pictures is always greater with Iodide of Cadmium than with Iodide of Potassium.

Selecting Cadmium, therefore, in preference to Potassium, let us consider two or three difficulties which the operator may have to encounter with it in hot climates. Supposing the plain Collodion and iodizer to have been sent out separately, it may happen that the preparation will give at first rather a foggy Negative; if so, keep it for a short time in the iodized state, and it will improve.

The next difficulty to be contended against is the redness and feeble quality of Cadmium Negatives taken in a bright light; the skies being usually solarized from over-action. The use of the Citric and Pyrogallic Acid developer (p. 164) is a remedy for this condition, and gives additional intensity of sky when the feebleness is due to over-action of light. In a hot climate such a developer ought to be strong enough to bring out the shadows, and it is of all the three formulæ (p. 287) the one most likely to give a Negative free from fogging. When the fogging and over-action of light appear to be caused by the neutral reaction of a film produced by Cadmium Collodion, the Writer remedies these defects by a solution of *Iodine* in Alcohol, one grain to the drachm, dropped into the Collodion until a clear yellow tint is produced: free Nitric Acid is then liberated on dipping the film in the Bath, and the employment of the Iodine is found to increase not only the clearness of the picture, but also the intensity: neither does it make much difference in the sensitiveness, if the light be good and the temperature high.

Mr. Sutton, of Jersey, has advocated the employment of a Collodion containing a far larger quantity of Alcohol than is usually preferred, viz. about three parts of Alcohol of sp. gr. ·805 to one part of Ether. It appears to the Writer that the ordinary proportions are better for our own climate, but that the Alcoholic Collodion would merit a fair trial when the rate of evaporation became excessive. Iodide of Cadmium is not in this case a suitable iodizer, from its tendency to gelatinize the Collodion in presence of excess of Alcohol. Any other Iodide would speedily liberate iodine when used alone, but a mixture of Iodide of Sodium (p. 125), Iodide of Ammonium, and Iodide of Cadmium, about $1\frac{1}{2}$ grains of each, with 1 grain of Bromide of Ammonium to prevent too speedy decomposition, would probably answer all requirements. The use of Bromides has indeed been tried in hot climates, and is reported upon most favourably.

A Photographer of experience, who has used simple iodides in hot countries, observes that the Nitrate Bath is liable to more rapid change than in England: it becomes acid, and requires constant neutralizing. May not this acidity be due to an oxidation of Ether or Alcohol at the expense of the Oxygen contained in the Nitrate of Silver?

On opening a box of Collodion which has been subjected to a high temperature in its transit, be careful to put it away at once in a dark place, since the fluid is probably in a state to *ozonize* rapidly by exposure to light, and in that case it would soon strike a brown colour with Iodide of Potassium. Negative Collodion which has arrived in India in a useless condition on account of this property of liberating Iodine, has been found very serviceable for taking Positives. To convert a Negative Collodion into one for Positives, see the directions at page 278.

Apparatus and Package.—Folding Cameras are not recommended for hot climates. The body of the instrument should be rigid and of substantial construction, bound with brass at the corners, and, if expense is not an object, panelled at the sides. The best mahogany thoroughly dried should be employed.

The Nitrate Bath, if of large size, may be carried in gutta-percha, as glass Baths are liable to be broken in the journey. A dipper, for instance, inadvertently left in the Bath, would probably crack it during the voyage.

The Writer has remarked that very expensive sets of Apparatus are sometimes sent abroad with a supply of Chemicals altogether inadequate; only a few ounces of Collodion being included, with a quantity of Nitrate of Silver barely sufficient to make a single Bath. The following list, corrected by the one given at page 328 for Landscape Photography, will be found to include all that is actually needed for the practice of the Negative Collodion and Printing Processes:—Collodion, 6 pints, with additional bromo-iodizer. Negative Nitrate Bath, 80 ounces. Nitrate of Silver for replenishing Bath and Printing, one pound. Two six-ounce bottles of transparent Varnish. Pyrogallic Acid, 1 ounce. Glacial Acetic Acid, one pound and a half. Citric Acid, 4 ounces. Absolute Alcohol, 12 oz. Pure Ether, 12 ounces. Spirits of Wine, 1 pint. Dry Carbonate of Soda, 8 ounces. Hyposulphite of Soda, 4 pounds. Cyanide of Potassium, 4 ounces. Papier Saxe, 2 quires. Filtering Paper, 2 quires. Chloride of Ammonium, 4 ounces. Chloride of Gold, 2 drachms. Liquor Ammoniæ, 2 ounces. Iodide of Potassium, ½ ounce. Iodide of Ammonium, ½ ounce. Tannic Acid, 2 ounces. Iodide of Cadmium, ½ ounce. Bromide of Ammonium, ½ ounce. Kaolin, 2 ounces. Tripoli, 2 ounces. Gallic Acid, 2 ounces. Albuminized paper for printing. Litmus paper.

Collodion should be sent in bottles well corked, and then tied over with bladder and dipped in hard cement; the stopper being fastened round the neck. This plan has been found to answer better than the most careful stoppering, or even capping outside the stopper with glass. The bottles ought not to be quite full, the heat causing expansion. As an additional security, fit each bottle into a tin box and pack it with sawdust.

In opening these bottles, be very careful to clean away the cement with the blade of a knife, as a portion of it sometimes finds its way into the Collodion.

Two or three spare dippers should be sent with the

Bath; also a piece of marine-glue for mending, and a spare focussing-glass. If both the focussing-glasses are broken, try Mr. Shadbolt's plan of substituting a piece of plain glass coated with iodized Collodion, sensitized, washed, and dried. This will show the image distinctly upon the surface of the Iodide of Silver.

Porcelain dishes are often broken in carriage: it may not be generally known that their place can be supplied by a sheet of ordinary Photographic paper folded into a tray and pinned up at the corners. Canson's Positive paper especially, will hold liquids for a long time: and if a more substantial piece of apparatus of the same kind be required, it may be made by passing a sheet of paper through a solution of gutta-percha in Benzole, and when it becomes dry, holding it to the fire so as to melt the little globules of gutta-percha into the paper, and render it impervious. Any paper may also be made to hold water by *parchmentizing* with Oil of Vitriol, as described at page 101, but the cockling up is an objection. A sheet of plate-glass let into a framework of wood, will form an excellent shallow tray for Nitrate of Silver, if the wooden sides be well dabbed with varnish to prevent absorption of the solution.

Albuminized paper sent out from England, has been found occasionally to decompose on the voyage. The eggs ought to be used quite fresh, and every sheet ironed to make it thoroughly dry before packing. Enclose the paper in a tin case soldered all round the edge to prevent it from taking the sea-water.

CHAPTER III.

THE PRACTICAL DETAILS OF PHOTOGRAPHIC PRINTING.

THIS Chapter is divided as follows:—

SECTION I.—The ordinary process of Positive printing.

SECTION II.—Positive printing by development, including the production of transparencies for the Stereoscope.

SECTION I.

Positive Printing by the direct action of Light.

The ordinary varieties of paper sold in commerce are not sufficiently smooth and uniform to be well adapted for the production of Positive prints, and even the finest papers prepared purposely for Photography are often defective. Hence each sheet should be examined separately by holding it against the light, and if *spots* or irregularities of texture are seen, it should be rejected. These spots usually consist of small particles of brass or iron, which, when the paper is rendered sensitive, decompose the Nitrate of Silver and leave a circular mark very noticeable after fixing.

The foreign papers, French and German, differ from the English in the mode of sizing adopted, and hence the two varieties will not produce similar tones, as already shown in Part I. In all cases there is a difference in smoothness between the two sides of the paper, which may be detected by holding each sheet in such a manner that the light strikes it at an angle; on the wrong side will be seen dark wavy bands, of an inch to an inch and a half in breadth, caused by the strips of felt on which the paper was dried. With most qualities of paper no difficulty whatever will be experienced in detecting the broad and regular bands above referred to; but when they cannot be seen, the wrong side of the sheet may be known by gauze wire markings; or, in default of such, the paper may be wetted at the corner, when one side will appear smoother than the other.

PREPARATION OF SENSITIVE PAPER.

There are three formulæ for sensitive paper, viz. the Albuminized, the plain, and the Ammonio-Nitrate paper.—

Formula I. *Preparation of Albuminized Paper.*—Take of

Chloride of Ammonium . . .	200 grains.
Water	5 fluid ounces.
Albumen	15 fluid ounces.

Chloride of Barium, sometimes used in salting paper instead of Chloride of Ammonium, is contra-indicated when the Alkaline Gold toning process is adopted, since the Carbonate of Soda would throw down Carbonate of Baryta in the paper.

When pure Albumen is used without water, from 5 to 8 grains of Salt to each ounce will be sufficient. The less the quantity of Salt the warmer the colour, but it must not be so far reduced as to injure the contrast and depth of shadow in the print.

If distilled water cannot be procured, rain-water or even common spring-water will often answer the purpose. For the Albumen, use eggs nearly fresh, and be careful that in opening the shell the yolk is not broken; each egg will yield about one fluid ounce of Albumen.

When the ingredients are mixed, take a bundle of quills or a fork, and beat the whole into a perfect froth. As the froth forms, it is to be skimmed off and placed in a flat dish to subside. The success of the operation depends very much upon this part of the process, for if the Albumen be not thoroughly beaten, flakes of animal membrane will be left in the liquid, and will cause streaks upon the paper. When the froth has partially subsided, transfer it to a tall and narrow jar, and allow to stand for several hours, that the membranous shreds may settle to the bottom. Then pour off the upper clear portion, which will be fit for use. Albuminous liquids are too glutinous to run well through a paper filter, and are better cleared by subsidence.

Another plan is to fill a bottle to about three parts with the salted mixture of Albumen and Water, and to shake it well for ten minutes or a quarter of an hour until it loses its glutinosity and can be poured out smoothly from the neck of the bottle: it is then to be transferred to an open jar, and allowed to settle as before. This method is more simple than the last, but is not so much used by makers of Albuminized paper.

Albumen alone, without any addition of water, gives a more highly varnished appearance, but much in this respect will depend upon the kind of paper employed, certain varieties of paper taking more gloss than others: on this subject consult the remarks made at page 181, of Part I.

The principal difficulty in Albuminizing paper, is to avoid the occurrence of streaky lines, which, when the paper is rendered sensitive, *bronze* strongly under the influence of the light. To avoid them, lower the paper on the liquid by one steady movement, since if a pause be made, a line will be formed. Some papers are not readily wetted by the Albumen, and when such is the case, a few drops of spirituous solution of bile, or a fragment of the prepared Ox-Gall sold by the artists'-colourmen, will be found a useful adjunct. Care must be taken however not to add an excess, or the Albumen will be rendered too fluid, and will sink into the paper, leaving no gloss. The Ox-Gall has been thought to make the paper tone more slowly in the Gold Bath, and consequently the Writer now omits it, and adds two drachms of Spirits of Wine (previously diluted with water to prevent coagulation) to each four ounces of Albumen. This removes the greasiness in a great measure, and lessens the chance of streaks.

In salting and Albuminizing Photographic paper by the formula above given, it is found that each quarter-sheet, measuring eleven inches by nine inches, removes one fluid drachm and a half from the Bath, equivalent to about one grain and three quarters of salt (including droppings). In salting plain paper, each quarter-sheet takes up only one drachm; so that the glutinous nature of the Albumen causes a third part more of salt to be retained by the paper.

English papers are apt to curl up when laid upon the liquid, and the process of toning the prints is slow. Hollingworth's thin paper, however, or Towgood's paper, will succeed with an active Toning Bath, and they have the merit of giving a bright and clear picture with good half-tone.

A paper was recently in the market made by Mr. Evans, of Nash Mills, Hemel Hempstead, and sized in a manner different from the English papers above described. It proved suitable for Albuminizing, and gave a red image in the printing frame. The proofs coloured rapidly in the Bath of Alkaline Chloride of Gold, and reached a dark tone. If this paper could be produced with a uniformly good sizing, equal to that of the sample forwarded to the Writer, it might safely be recommended.

The thin Negative Paper of Canson, the Papier Rive, and Papier Saxe, have in the Writer's hands given better results than Canson's Positive Paper, which until recently was much used.

To apply Albumen, pour a portion of the solution into a flat dish to the depth of half an inch. Then, having previously cut the paper to the proper size, take a sheet by the two corners, bend it into a curved form, convexity downwards, and lay it upon the Albumen, the centre part first touching the liquid, and the corners being lowered gradually. In this way bubbles of air will be pushed forwards and excluded. One side only of the paper is wetted: the other remains dry. Allow the sheet to rest upon the solution for *one minute and a half*, and then raise it off, and pin it up by two corners. If any circular spots, free from Albumen, are seen, caused by bubbles of air, replace the sheet for the same length of time as at first.

The paper must not be allowed to rest upon the Salting Bath much longer than the time specified, because the solution of Albumen being *alkaline* (p. 188), tends to remove the size from the paper and to sink in too deeply: thus losing its surface gloss.

Albuminized paper will keep a long time in a dry place. Some have recommended to press it with a heated iron, in order to coagulate the layer of Albumen upon the surface; but this precaution is unnecessary, since the coagulation is perfectly effected by the Nitrate of Silver used in sensitizing; and it is doubtful whether a layer of *dry* Albumen admits of coagulation by the simple application of a heated iron.

In cutting the paper to the required sizes use a *bone* spatula, and avoid touching the Albuminized surface with the fingers. Press the sheets flat between boards, or in a printing frame, and if possible avoid rolling them.

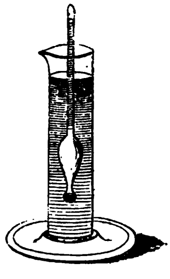
To render the paper sensitive.—This operation must be conducted by the light of a candle, or by yellow light. Take of

Nitrate of Silver	60 grains.
Distilled Water	1 ounce.

Prepare a sufficient quantity of this solution, and pour it out into a porcelain dish. After it has been a short time in use, the Albumen dissolved out of the papers will cause a greasy scum to form upon the liquid, which if allowed to remain produces marbled stains upon the sensitive paper; it must therefore be removed by folding a strip of blotting-paper the exact breadth of the dish, and drawing it lightly along the surface. Lay the sheet upon the solution in the same manner as above described for the Albumen. Three minutes' contact will be sufficient with thin paper, but if a thick paper be used, four or five minutes must be allowed for the decomposition. The papers are raised from the solution by a pair of bone forceps, or common tweezers tipped with sealing-wax; or a pin may be used to lift up the corner, which is to be held by the finger and thumb and allowed *to drain a little* before again putting in the pin, otherwise a white mark will be produced upon the paper, from decomposition of the Nitrate of Silver. When the sheet is hung up, a small strip of blotting-paper suspended from the lower edge of the paper will serve to drain off the last drop of liquid.

A Bath prepared by the above formula is stronger than is actually necessary. Forty-five or fifty grains of pure Nitrate to the ounce of water would be sufficient; but it must be borne in mind that the strength of the Bath diminishes *rapidly* by use, and hence, when the prints begin to be wanting in vigour, with pale shadows and perhaps a spotted appearance, an addition of Nitrate of Silver must be made.

The following little piece of apparatus, known as a "Silver Meter," is now almost universally employed.



It consists of a cylindrical vessel holding some two or three ounces, with an hydrometer of the common form. The Sensitizing Bath to be tested is poured into the glass, and the bulb floated in it, when the number of grains per ounce will be indicated by the part of the scale corresponding to the surface of the liquid. As these instruments are sold for a few shillings, and consequently are not made with much care, it is advisable to commence by preparing a 60-grain solution of pure Nitrate of Silver, to verify the correctness of the scale. Observe also that the indications of the hydrometer will cease to be trustworthy if the Bath contain Alcohol or Ether: hence an old Negative Bath, properly analyzed, will be found to yield three or four grains of Nitrate per ounce, over the quantity given by floating.

The solution of Nitrate of Silver becomes after a time discoloured by the Albumen, but may be used for sensitizing until it is nearly black. The colour can be removed by Animal Charcoal,* but a better plan is to use the "Kaolin," or pure white china clay. Shake up twenty ounces of Bath with a quarter of an ounce of finely pulverized Kaolin, and filter through paper. Kaolin often contains Carbonate of Lime, and effervesces with acids: if so, it must be purified by washing in dilute vinegar, or the Bath will become alkaline, and dissolve off the Albumen. It is stated that an addition of Alcohol to the Nitrate Bath prevents it from discolouring with Albumen.

When Kaolin cannot be obtained, the Bath may be decolorized by shaking it up with recently precipitated Chloride of Silver in the curdy state. This substance has an affinity for the brown Sub-Albuminate of Silver which produces the colour, and gradually carries it down, leaving the supernatant liquid clear; but it is inferior to Kaolin as a decolorizer.

Old printing Nitrate Baths often become somewhat alkaline from the reaction of the Albumen; and the proportion of Silver falls so low that the coagulation of the Albumen is imperfect, and a white precipitate falls away into the Bath. In such a case add to each ounce ten grains of Nitrate of Silver, and half a drop of Glacial Acetic Acid.

Sensitive albuminized paper will usually remain good for several days, if protected from the light, but it afterwards turns yellow from partial decomposition. To preserve the sheets white for a longer time, dry them in a warm place, and then pile them up under pressure in a printing-frame: this excludes the air, and is a better plan than that of placing the papers between the leaves of a book, since, as shown at page 52, the printers' ink may gradually produce an effect upon the surface. For a description of a drying apparatus intended to preserve sensitized papers for an indefinite time, see page 190. Papers so kept however can scarcely be considered equal to those recently sensitized.

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* Common Animal Charcoal contains Carbonate or Phosphate of Lime, the former of which renders the Nitrate of Silver *alkaline*; purified Animal Charcoal is usually acid from Hydrochloric Acid.

Formula II. *Preparation of Plain Paper.*—Take of

Chloride of Ammonium	200 grains.
Citrate of Soda	200 grains.
Gelatine	20 grains.
Water	20 ounces.

To prepare the Citrate of Soda, dissolve 112 grains of Citric Acid in the 20 ounces of Water, and add 133 grains of the dried Bicarbonate or Sesquicarbonate of Soda used for effervescing draughts. Supposing the Citric Acid to be adulterated with Tartaric Acid, the above quantity of Carbonate of Soda would be too great, and free alkaline Carbonate would then remain in the liquid after the neutralization was complete. The size of the paper would be liable to suffer in such a case, and the print would not be clean and bright. Excess of Citric Acid, on the other hand, gives very clean pictures, but they are too pale and red, without depth of shadow. Amateurs desirous of simplifying the formula may substitute an equal weight of "Rochelle Salt" for the Citrate of Soda: this substance is a Tartrate of Potash and Soda, and is sold by druggists in large crystals. A reference to Part I., page 189, will show that both Tartrates and Citrates are used for the purpose of giving a red and warm tone to the prints.

Use Papier Saxe, or Towgood's or Hollingworth's paper, for the above formula, each sheet being floated for one minute, and then suspended to dry as directed for albuminized paper. It is doubtful whether salted papers containing Tartrate and Citrate are to be depended upon for long keeping, since in presence of moisture these organic salts become mouldy, and absorb Oxygen from the air.

Render sensitive by floating for two or three minutes upon the solution of Nitrate of Silver employed for the *Albuminized* paper.

Formula III. *Ammonio-Nitrate Paper.*—This is always prepared without Albumen, which is dissolved by Ammonio-Nitrate of Silver. Take of

Chloride of Ammonium	40 grains.
Gelatine	20 grains.
Water	20 ounces.

Dissolve by the aid of heat, and filter when cold.

Take ten or a dozen sheets of thin Hollingworth's or Towgood's paper, and having marked the right side, immerse them bodily in the liquid, one by one, with care to remove air-bubbles. Then turn the batch over and remove them singly, beginning with the sheet first immersed. Each paper will thus be a similar length of time in the salting liquid.

This salting solution is very weak, but it must be borne in mind that the papers being *immersed* will take up a larger quantity (p. 182), and also that the Ammonio-Nitrate process requires less salt, inasmuch as the Silver solution is to be laid on with a brush.

An Ammonio-Nitrate paper yielding a very rich colour is made by salting Towgood's paper, or Papier Saxe, with a mixed Chloride and Citrate, in quantity exactly *one-half* of that advised in the last page, and afterwards sensitizing it with an 80-grain solution of Ammonio-Nitrate. The Writer however gives a formula with a smaller quantity of salt in preference; having found that beginners cannot *brush* a highly salted paper sufficiently evenly to prevent marks on the finished picture.

Render sensitive by a solution of Ammonio-Nitrate of Silver, 60 grains to the ounce of water, prepared as follows:—

Dissolve the Nitrate of Silver in one-half of the total quantity of water. Then take a pure solution of Ammonia and drop it in carefully, stirring meanwhile with a glass rod. A brown precipitate of Oxide of Silver first forms, but on the addition of more Ammonia it is redissolved.*

* If the excess of Ammonia does not readily dissolve the precipitate, probably the Nitrate of Silver is impure.

When the liquid appears to be clearing up, add the Ammonia very cautiously, so as not to incur an excess. In order still further to secure the absence of free Ammonia, it is usual to direct that, when the liquid becomes perfectly clear, a drop or two of solution of Nitrate of Silver should be added until a *slight turbidity* is again produced. Lastly, dilute with water to the proper bulk. If the crystals of Nitrate of Silver employed contain a large excess of free Nitric Acid, no precipitate will be formed on the first addition of Ammonia: the free Nitric Acid, producing *Nitrate of Ammonia* with the alkali, keeps the Oxide of Silver in solution. This cause of error however is not likely to happen frequently, since the amount of Nitrate of Ammonia required to prevent all precipitation would be considerable. From the same reason, viz. the presence of Nitrate of Ammonia, it is often useless to attempt to convert an old Nitrate Bath already used for sensitizing, into Ammonio-Nitrate.

The great objection to the use of Ammonio-Nitrate of Silver, as above prepared, is the liberation of free Ammonia in sensitizing the salted papers. To obviate this in a measure, the Author employs *Nitrate of Ammonia* as the solvent for the Oxide of Silver. The solution is prepared as follows:—Dissolve 60 grains of Nitrate of Silver in half an ounce of water, and drop in Ammonia until the precipitated Oxide of Silver is exactly re-dissolved. Then divide this solution of Ammonio-Nitrate of Silver into two equal parts, to *one* of which add Nitric Acid cautiously, until a piece of immersed litmus-paper is reddened by an excess of the acid; then mix the two together, fill up to one ounce with water, and filter from the milky deposit of Chloride or Carbonate of Silver, if any be formed.

Ammonio-Nitrate of Silver should be kept in a dark place, being more prone to reduction than the Nitrate of Silver.

To apply the liquid.—It is not usual to *float* the paper when the Ammonio-Nitrate of Silver is used, for reasons given at page 187. Brushes are manufactured purposely for applying Silver solutions, but the hair is soon destroyed unless the brush be kept scrupulously clean. Lay the salted sheet upon blotting-paper, and wet it thoroughly by drawing the brush first lengthways and then across. Allow it to remain flat for a minute or so, in order that a sufficient quantity of the solution may be absorbed (you will see when it is evenly wet by looking along the surface), and then pin up by the corner in the usual way. If, on drying, *white lines* appear at the points last touched by the brush, it is probable that the paper was too highly salted, or that the Ammonio-Nitrate contained free Ammonia.

Ammonio-Nitrate paper is more prone to spontaneous decomposition than either Albuminized or plain paper; hence it cannot be kept many hours after sensitizing without turning yellow.

PREPARATION OF THE TONING BATH.

Two formulæ may be given, differing but little in their mode of action, or in the tones which they yield. The first is the more generally employed; but the second, proposed by Mr. Maxwell Lyte, has also many advocates, and is considered by some to produce a warmer shade of colour.

No. 1.	Solution of Chloride of Gold . .	1 fluid drachm.
	Sesquicarbonate of Soda . . .	10 grains.
	Distilled Water	6 fluid ounces.
No. 2.	Solution of Chloride of Gold . .	1 fluid drachm.
	Ordinary Phosphate of Soda .	20 grains.
	Distilled Water	2 fluid ounces.

The best Chloride of Gold to use for these formulæ is that from which the excess of Hydrochloric Acid has been nearly driven off by repeated evaporations to dryness on a water bath. In commerce however this comparatively neutral Chloride can rarely be obtained, and even the "Chloride of Gold and Sodium," sold as a neutral salt, will often be found on testing to be very acid. It is therefore advisable in the case of Formula 2 to examine the Chloride of Gold, and if its solution immediately colours litmus-paper *of a bright red,* to add to each grain a fragment of Carbonate of Soda about the size of a pin's head.

The solution of Chloride of Gold contains a grain to each fluid drachm of water, and will keep for an unlimited time without appreciable change, previously to the addition of the Carbonate of Soda. The toning baths, however, must not be kept ready mixed, since they gradually become colourless, and eventually lose their toning properties in great measure. A useful simplification, substituting measure for weight, consists in having always on hand an aqueous solution of Carbonate of Soda containing twenty grains to the ounce, or, for the second formula, a solution of Phosphate of Soda containing forty grains to the ounce. Half an ounce of the alkaline liquid would then in each case require a fluid drachm of the solution of Chloride of Gold, and a subsequent dilution with water to the full amount given in the formula.

When the toning bath is to be used soon after mixing, the Writer prefers to add the Gold to the concentrated alkaline solution, and to allow a few minutes to elapse before diluting; the object being to hasten the conversion of a portion of the Chloride into Oxide of Gold, and thus to diminish the tendency to eat away the delicate parts of the proof.

THE FIXING BATH.

Take of—

Hyposulphite of Soda	1 ounce.
Water	6 ounces.

Dissolve without filtering, and preserve the solution in a stock bottle ready for use.

MANIPULATORY DETAILS OF PHOTOGRAPHIC PRINTING.

Sensitive papers ought not to be exposed in the frame until they are quite dry, on account of the danger of staining the Negative with Nitrate of Silver. It will often be convenient to dry the paper rapidly by the heat of a fire, or by a metal plate placed over a lamp, which may be done without fear even in ordinary daylight. Ammonio-Nitrate paper, however, will require a little extra care in this respect.

Paper thus dried should always be allowed ten minutes or longer to become cold before putting it into the printing-frame, otherwise it will cockle up and form ridges beneath the Negative.

The Exposure to Light.—For this purpose reversing-frames are sold, which admit of being opened at the back, in order to examine the progress of the darkening by light, without producing any disturbance of position. Simple squares of glass however succeed equally well, when a little experience has been acquired. They may be held together by the wooden clips sold at the American warehouses at a shilling per dozen. The lower plate should be covered with black cloth or velvet.

Supposing the frame to be employed, the shutter at the back is removed, and the Negative laid flat upon the glass, Collodion side uppermost. A sheet of sensitive paper is then placed upon the Negative, sensitive side downwards; next comes a layer of thick felt; and the whole is then tightly compressed by replacing and bolting down the shutter. The amount of pressure required is not very considerable, but if the springs of the frame become too weak after a time, a few pieces of mill-board may be placed beneath them.

This operation may be conducted in the dark room; but unless the light is very strong, such a precaution will be needless. The time of exposure to light varies much with the density of the Negative and the power of the actinic rays, as influenced by the season of the year and other obvious considerations. As a general rule, the best Negatives print rather slowly; whereas Negatives which have been under-exposed and under-developed print quickly.

In the early spring or summer, when the light is powerful, about ten to fifteen minutes may be required; but from three-quarters of an hour to an hour and a half may be allowed in the winter months, even in the direct rays of the sun. It is always easy to judge of the length of time which will be sufficient, by exposing a small slip of the sensitive paper, unshielded, to the sun's rays, and observing how long it takes to reach the coppery stage of reduction. Whatever that time may be, nearly the same will be occupied in the printing, if the Negative be a good one.

In a dull London light the Writer has seen four days spent in getting one impression from a Negative ; but pictures so obtained are not equal to others printed by a stronger light. The organic matter of the size reacts more or less upon the Nitrate of Silver, and causes yellowness of the whites of the paper: the toning process is also interfered with, as will presently be shown.

A light of excessive brilliancy is objectionable in printing, and especially so when the thermometer stands high. Complaints of unmanageable bronzing, with obliteration of details in the shadows, are frequent at such times, the reducing process being carried on with too much activity. Hence it is sometimes advisable, in the summer months, not to print by the direct rays of the Sun. This point is further important, because the excessive heat of the Sun's rays often cracks the glasses by unequal expansion, and glues the Negative firmly down to the sensitive paper. An exception may be made in the case of Negatives of great intensity, which are printed most successfully upon a weakly sensitized paper (p. 183) exposed to the full rays of the Sun; a feeble light not fully penetrating the dark parts.

When the darkening of the paper appears to have proceeded to a considerable extent, the frame is taken in and the picture examined. This, however, may be done in the open air, with care and expedition. If squares of plate glass are used to keep the Negative and sensitive paper in contact, some difficulty may be experienced at first in returning it precisely to the same position after the examination is complete, but it will be overcome by practice. The finger and thumb should be fixed on the lower corners or edge, and the plate raised evenly and quickly.

If the exposure to light has been correct, the print appears *slightly darker* than it is intended to remain. The toning Bath dissolves away the lighter shades, and reduces the intensity, for which allowance is made in the exposure to light. A little experience soon teaches the proper point; but much will depend upon the state of the Toning Bath, and albuminized paper will require to be printed somewhat more deeply than plain paper.

If, on removal from the printing-frame, a peculiar *spotted* appearance is seen, produced by unequal darkening of the Chloride of Silver, either the Nitrate Bath is too weak, the sheet removed from its surface too speedily, or the paper is of inferior quality.

On the other hand, if the general aspect of the print is a rich chocolate-brown in the case of Albumen, a dark slate-blue with Ammonio-Nitrate Paper, or a reddish-purple with paper prepared with Chloride and Citrate of Silver, or Chloride and Serum of Milk, the subsequent parts of the process will probably proceed well.

If, in the exposure to ordinary diffused daylight, the shadows of the proof became very decidedly *coppery* before the lights are sufficiently printed, the Negative is in fault. Ammonio-Nitrate paper highly salted is particularly liable to this excess of reduction, and especially so if the light is powerful.

The Toning of the Proof.—No injury results from postponing this part of the process for some hours, provided the print be kept in a dark place. But it is not advisable to leave the print for several days before toning, since a chemical change may take place, the effect of which will be to interfere with the deposition of the Gold in the toning process. It is considered that more harm is done by keeping paper after printing, than by keeping it between sensitizing and exposure.

The print should be first washed in common water until the soluble Nitrate of Silver is removed. This is known to be the case when the liquid flows away clear; the first milkiness being caused by the soluble Carbonates and Chlorides in the water precipitating the Nitrate of Silver. Ten minutes in water running slowly from a tap will be sufficient to cleanse a print from Nitrate of Silver; or three or four changes in a dish, pouring off quite dry between each change. A difference of opinion exists as to the use of a final Bath of Salt and Water to convert the last traces of Nitrate into Chloride of Silver. Most operators content themselves with simple Water, but the Writer believes that it is an advantage to finish off with solution of Salt (two grains to the ounce), in cases where the printing has not been carried far enough; the half-tints are better preserved thereby from the destructive action of the Chlorine contained in the Gold solution, and the colour is not so likely to disappear in the fixing Bath.

A white sediment often forms upon the prints if they are left too long in hard water without moving. The sediment consists of Carbonate and Chloride of Silver, and would be dissolved by treatment with water smelling very faintly of free Ammonia. The fixing Bath however will clear it away in great measure, leaving only a slight want of brilliancy on drying.

Pour the toning Bath out into a flat dish and put the prints into it two or three at a time, waving the dish meanwhile backwards and forwards to secure a constant movement. The danger is that the prints will project above the surface of the liquid, or that they will stick together; the result in both cases being a large red spot of imperfect toning. Continue to keep the prints moving, and watch the changes in colour. At first the toning will be complete in two or three minutes; then, as the proportion of Gold falls, in five minutes; afterwards in ten minutes or a quarter of an hour.

The action of the Bath must be regulated according to the colour desired. If the Prints are removed as soon as the blue colour of the Gold is seen, they will usually change in the fixing Bath to a warm shade of brown; but when left for two or three minutes longer in the toning Bath, the darker tint becomes permanent. Hold them up against the light, and when they cease to appear red by transmission, the colour is well fixed upon the image and they are ready for the Hyposulphite.

Overprinted proofs always yield the blackest colours, because they may be kept for a longer time in the Gold without losing the half-tones: and, indeed, the state of the lighter shades of the proof is a good criterion of the time for removing it, since the Chlorine previously combined with the Gold has a bleaching action.

Do not attempt to get pure black and white tones on pictures printed from a feeble Negative. Unless there be a perceptible amount of bronzing, the deep blacks cannot be obtained on albuminized paper. The ultimate colour of the Print will also vary much with the density of the Negative and the character of the subject: copies of line engravings having but little half-tone, are easily obtained of a dark shade resembling the original impression.

Each grain of Chloride of Gold ought to tone seven or eight pictures of the stereoscopic size without any difficulty, or even a larger number if the Bath be used until it is entirely exhausted. Mr. C. Jabez Hughes, who has devoted much attention to this process, states that one grain of Chloride of Gold will tone five hundred square inches, or twenty stereoscopic pictures.

The most common error with beginners is to leave the prints too long in the toning Bath, in which case they appear blue and inky after fixing, without any depth of shadow. Sometimes however the opposite error prevails, and the prints having been removed too speedily, the Hyposulphite leaves them of a brick-red hue.

The observations given above apply principally to albuminized paper, which is far more generally employed than plain paper. Plain paper prints tone with greater facility than prints upon Albumen, and hence it may be desirable to dilute the alkaline Chloride of Gold with water, if the action of the Bath should prove uncontrollable.

In toning prints by alkaline Chloride of Gold, it is not necessary to work entirely in the yellow room, but a subdued light is usually recommended.

Washing in water between the toning and fixing is not required; the proofs may be passed from the one Bath to the other. In doing this, however, there is great danger that the fingers will convey a little of the Hyposulphite fixing Bath into the toning Bath, and if so, the Chloride of Gold will be decomposed, and the toning action thereby suspended. A pair of horn forceps should be kept in the fixing Bath, and each print as it is removed from the toning solution with the left hand should be seized by the forceps held in the right hand, and be immediately immersed in the Hyposulphite solution.

An ounce of Hyposulphite of Soda dissolved in six ounces of Water would fix two batches of stereoscopic prints, twenty in each batch. The solution however may be thrown away when twenty prints have been immersed in each six ounces of Bath, since the price of Hyposulphite of Soda is very small, and it is not worth while to risk the occurrence of yellow patches of imperfect fixation. Allow the prints to remain in the fixing Bath for twenty minutes, with occasional movement, after which they may be transferred to a dish of clean water.

A newly prepared fixing Bath will usually lower the tone of the prints more or less, and this even although a strong deposit of Gold exists upon the image. The weaker the solution of the Hyposulphite, the less the lowering action, and the greater the probability that the slight loss of colour at first perceived, will return on drying the print. Solutions of Hyposulphite which are used over and over again (fresh crystals of Hyposulphite being occasionally added, until the specific gravity is found to be correct by the hydrometer), acquire by degrees a slight sulphuretting property which much improves the colour of the print. This mode of working is adopted by some: but, on theoretical grounds, the plan of making a fresh bath each day is better (p. 204).

The washing, drying, and mounting of the Positive Proofs.—It is essential to wash out every trace of Hyposulphite of Soda from the Print if it is to be preserved from fading, and to do this properly requires care.

Always wash with *running water* when it can be obtained, and choose a large shallow vessel exposing a considerable surface in preference to one of lesser diameter. A constant dribbling of water must be maintained for four or five hours, and the prints should not lie together too closely, or the water will not find its way between them (p. 205).

The most perfect apparatus which the Writer has seen for washing prints on a large scale, consisted of a series of circular troughs, about a yard wide and twelve inches deep, with a small siphon in each, so arranged that when the water rose to the bend of the tube, the siphon at once began to act, and gradually drew it off dry. Twice during the day, when the water came on from the main, it was allowed to flow freely through the troughs, and being directed by a tube against the sides, the prints were kept spinning round, and a constant change of water was thus secured. It would not be safe to make such troughs of Zinc or any common metal, unless a glaze were applied to the interior, since Hyposulphite charged with Salts of Silver gradually acts upon Zinc.

When running water cannot be obtained, proceed as follows:—First wash the Prints gently, to remove the greater part of the Hyposulphite solution. Then transfer them to a large shallow pan, in which may be placed as many Prints as it will conveniently hold. Leave them in for about a quarter of an hour, with occasional movement, and then *pour off the water quite dry*. This point is important, viz. to drain off the last portion of liquid completely before adding fresh water. Repeat this process every half-hour, giving five or six changes, or more, according to the bulk of water, number of Prints, and degree of attention paid to them.

Dabbing with a large sponge has been recommended for cleansing prints from Hyposulphite. A quarter of an hour's application of this kind goes further than two or three hours of washing, since the suction power of a sponge draws out the liquid from the substance of the paper.

Lastly, proceed to remove the size from the print by immersion in hot water.* Ammonio-Nitrate and plain paper Prints prepared on foreign papers may be expected to stand the test of boiling water; Albumen Prints and Positives on English paper are a little reddened, although not to an objectionable degree.

The treatment of prints with hot water is a plan which all approve theoretically, but few adopt; the Writer however does not esteem a print secure unless it has been immersed in water nearly at the boiling point.

When the prints have been thoroughly washed, blot them off between sheets of porous paper and hang them up to dry. Some press them with a hot iron, which darkens the colour slightly, but not in an injurious manner, unless Hyposulphite of Soda remains in the paper. This darkening by dry heat is most evidently seen in the case of English papers sized with Gelatine, and sensitized by Ammonio-Nitrate of Silver.

Albumen proofs when dry are sufficiently bright without further treatment; but in the case of plain paper, salted simply, the effect is improved by laying the Print face downwards upon a square of plate-glass and rubbing the back with an agate burnisher, sold at the artists'-colourman's. This hardens the grain of the paper and brings out the details of the picture. Hot-pressing has a similar effect, and is often employed.

Mount the proofs with a solution of Gelatine in hot water, freshly made; the best Scotch glue answers well. Gum-water, prepared from the finest commercial gum, and free from acidity, may also be used, but it should be made very thick, so as not to sink into the paper, or produce "cockling up" of the cardboard on drying.

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* The Print must be well washed in cold water, to remove the Hyposulphite, before using the hot water; otherwise the half-tones will be liable to be darkened, or changed to incipient yellowness, by sulphuration. This point is important as regards the permanency.

Caoutchouc dissolved in mineral Naphtha to the consistence of thick glue or gold-beaters' size, is employed by some for mounting Photographic Prints; it may be obtained at the varnish-shops, and is sold in tin boxes. The mode of using it is as follows:—With a broad brush made of stiff bristles, apply the cement to the back of the picture: then take a strip of glass with a straight edge, and by drawing it across the paper, scrape off as much as possible of the excess. The print will then be found to adhere very readily to the cardboard, without causing expansion or cockling; and any portion of the cement which oozes out during the pressing may, when dry, be removed with a penknife without leaving a stain.

VIGNETTING.

This mode of printing, by which the edges of the Photograph are softened away, produces a very agreeable effect. Attempts have been made to obtain the result by placing in front of the Negative a plate of tinted glass, having the colour stippled in gradually from the edges, so as to leave the centre quite transparent. Some of the glasses made in that way are very good, but often the gradation is imperfect, and the print in consequence shows an abrupt margin.

The use of Cotton-wool has been recommended for printing vignettes, but it requires dexterity to arrange it. The following plan is more simple. Take a sheet of mill-board or coloured card, and cut out from the centre an aperture decidedly smaller than the picture required. The shape of this aperture may be varied at pleasure, but for portraits nothing is better than an oval, or the same expanded below into a triangular-shaped outline. Fasten this screen to the front part of the printing-frame, at a distance of about three-quarters of an inch, and expose in the ordinary way. The direct rays of the sun must be avoided, and the print should be placed in a shady place, when the light will diffuse itself evenly, and a perfect softening will be produced to an extent varying with the size of the aperture and its distance from the front glass. The strength of the light is to be considered in determining the size of the aperture; and in whatever direction the light falls, the frame should be placed at right angles to it.

SECTION II.

Positive Printing by Development.

Negative printing processes will be found useful during the dull winter months, and at other times when the light is feeble, or when it is required to produce a large number of impressions from a Negative in a short space of time. The proofs however as thus obtained are not equal to direct sun-prints in beauty and gradation of tone.

In the present Edition two methods are described, of which the first is more suitable when a luminous image of low intensity is to be projected upon the prepared paper, and the second may be preferred for printing beneath a Negative in the ordinary way.

A NEGATIVE PRINTING PROCESS UPON IODIDE AND BROMIDE OF SILVER.

Iodide of Silver is more sensitive to the reception of the invisible image than the other compounds of that metal; and hence it is usefully employed in printing *enlarged* Positives from small Negatives, by means of the solar Camera. The great stability of the proofs upon Iodide of Silver will also be a recommendation of this process when unusual permanency is required.

Take of

Iodide of Potassium . . .	120 grains.
Bromide of Ammonium . .	30 grains.
Water	20 fluid ounces.

The best paper to use will be either Turner's Calotype, or Whatman's or Hollingworth's Negative; the foreign papers do not succeed well with the above formula

Float the paper on the iodizing Bath until it ceases to curl up, and lies flat upon the liquid: then pin up to dry in the usual way.

Render sensitive upon a Bath of Aceto-Nitrate of Silver containing 30 grains of Nitrate of Silver with 30 minims of Glacial Acetic Acid to each ounce of water.

When the process is to be used for printing beneath a Negative, place the dried sheet in contact with the Negative in a pressure frame, and expose *to a feeble light.* About 30 seconds will be an average time upon a dull winter's day, when it would be impossible to print in the ordinary way. On removing the Negative nothing can be seen upon the paper, the image being strictly invisible in this process, unless the exposure has been carried too far.

Develope by immersion in a saturated solution of Gallic Acid prepared as described under the head of "Collodio-Albumen dry process." The image appears slowly, and the process may last from fifteen minutes to half an hour. If the exposure has been correctly timed, the Gallic Acid appears at length almost to cease acting; but when the proof has been over-exposed, the development goes on uninterruptedly, and the image becomes too dark, partaking more of the character of a Negative than a Positive, and disappearing from the surface. The usual rule, that *under*-exposed proofs develope slowly but show no half-tones, and that the *over*-exposed develope with unusual rapidity, is observed in the process with Iodide of Silver.

After the picture is fully brought out, wash in cold, and subsequently in warm water, to remove the Gallic Acid, which, if allowed to remain, would discolour the Hyposulphite Bath. Fix the Print in a solution of Hyposulphite of Soda, one part to two of water, continuing the action until the yellow colour of the Iodide disappears. The fixing Bath ought not to produce much change in the tint. If the Positive loses its dark colour on immersion in the Hyposulphite, and becomes pale and red, it has been insufficiently developed and probably too much exposed.

The colour of Positives developed upon Iodide and

Bromide of Silver is not very agreeable, but by fixing the proof in Hyposulphite of Soda which has been long used and has acquired sulphuretting properties, the tint is somewhat improved.

NEGATIVE PRINTING PROCESS UPON CHLORIDE OF SILVER.

Positives may be obtained by exposing ordinary Chloride of Silver Paper to the action of light until a faint image is perceptible, and subsequently developing it by Gallic Acid. It is difficult however to obtain sufficient *contrast* of light and shade in this way; the impression, if sufficiently exposed and not too much developed, being feeble, with a want of intensity in the dark parts. By associating with the Chloride an organic salt of Silver, such as the Citrate, this difficulty may be overcome, and the shadows brought out with great depth and distinctness.

The formula now given is the best known to the Writer, but he cannot recommend it with full confidence. All Negative paper processes appear to be greatly dependent upon the quality of the paper used, and it is not easy to obtain Photographic paper uniformly good. Hence result such defects as a sunk-in appearance of the picture, and a poverty of tone, which would not occur with a paper sized in a different way. It will be better that the operator should not attempt Negative printing until he feels himself to be a perfect master of the Art.

To salt the papers, prepare the following solution :—

Chloride of Ammonium	100 grains.
Citric Acid	56 grains.
Sesquicarbonate of Soda	66 grains.
Gelatine	40 grains.
Distilled Water	20 ounces.

The effervescing Carbonate of Soda sold by druggists is the compound to be used, and the Citric Acid must be genuine, not adulterated with Tartaric Acid (see Vocabulary). Choose the Papier Saxe in preference to any other paper, and float the sheets for one minute, after which they may be pinned up in the usual way.

This salting solution is liable to decompose by keeping, since Citrates become mouldy in presence of Gelatine. Alcohol 1½ ounce with two drops of Oil of Cloves dissolved would tend to preserve it. Complaints have also been made of the salted paper decomposing by keeping. To obviate this, hold each sheet to the fire before packing it away, and keep the paper in a very dry place.

Render sensitive upon a Bath of Aceto-Nitrate of Silver prepared in the same way as for the Collodio-Albumen dry process; and the proper management of which is described in the Fifth Chapter.

Take of

Nitrate of Silver	30 grains.
Glacial Acetic Acid	30 minims.
Water	1 fluid ounce.

Float the papers upon this Bath for three minutes, and suspend them to dry in a room from which actinic rays are *perfectly* excluded.

The exposure to light is conducted in the ordinary printing frame, the Negative and sensitive paper being laid in contact in the usual way, and it will seldom be longer than three or four minutes, even upon a dull day. It may be regulated by the colour assumed by the projecting margin of the paper; but it is quite possible to tell by the appearance of the image when it has received a sufficient amount of exposure. The whole of the picture should be seen, excepting the lightest shades, and it will be found that comparatively few details can be brought out in the development which were altogether invisible before the Gallic Acid was applied.

The developing solution is prepared as follows:—

Gallic Acid	2 grains.
Water	1 fluid ounce.

Filter through blotting-paper to remove floating particles, which would produce spots in this process.

To facilitate the solution of the Gallic Acid, stand the bottle in a warm place near the fire. A lump of Camphor floated in the liquid, or a drop of Oil of Cloves added, will to a great extent prevent it from becoming mouldy by keeping; but if once mould has formed, the bottle must be well cleansed with Nitric Acid, or the decomposition of the fresh Gallic Acid will be hastened.

When the weather is cold and the light bad, the development of the image proceeds slowly, the Gallic Acid Bath remains clear, and good half-tones are obtained: but under opposite conditions, the developer may become turbid and the shadows be lost by excessive deposit of Silver. This *over-development* will be remedied by printing the Negative in a feeble light (near to the open window of a room), and by adding Acetic Acid to the developer, about five or ten minims to the ounce, so as to bring out the image more slowly.

Pour the solution of Gallic Acid into a flat dish, and immerse the prints two or three at a time, moving them about, and using a glass rod to remove air-bubbles. The development will probably be completed in from three to six minutes. If the Print developes slowly, becoming after a time *very dark in colour*, but showing no half-tones, it has not been exposed sufficiently long to the light. An *over*-exposed proof, on the other hand, developes with unusual rapidity, and it is necessary to remove it speedily from the Bath in order to preserve the clearness of the white parts; when taken out to the light, it appears pale and red, with no depth of shadow.

A saving of Gallic Acid may be effected by adopting a plan of which the Writer was informed by Mr. Sutton, of Jersey. It consists in turning up the edges of the paper all round, so as to make the print its own developing dish. No pinning at the corners will be needed, and the solution of Gallic Acid may be spread by means of a glass rod bent at right angles. Lay each print upon a plate of glass, to prevent the back from being soiled. The paper ought not to be of a kind which is given to cockling, or portions of the image will rise above the level of the liquid. Bear in mind that the development will be unusually rapid and intense when this mode of manipulating is followed; inasmuch as the Nitrate of Siver is all retained in the picture, and the quantity of Gallic Acid is relatively small. Hence an addition of Acetic Acid may be needed as before advised.

The extent to which the development should be carried depends upon the kind of Print desired. By pushing the action of the Gallic Acid, a dark picture not much altered by the fixing Bath will be produced. But a better result as regards colour and gradation of tone will be obtained by removing the Print from the developing solution whilst in the light-red stage, and toning it subsequently by means of Gold; in which case it will correspond very much both in appearance and stability to a Positive obtained by the direct action of light (p. 54).

When it is intended to follow the latter plan, the action of the developer must be stopped at a point when the proof appears lighter than it is to remain; since the Gold Bath adds a little to the intensity, and the image becomes somewhat more vigorous on drying.

Wash the Prints for several minutes in one or two changes of water, in order to extract the Gallic Acid; which if allowed to remain will discolour the toning Bath. Sometimes the developing action of the Gallic Acid will continue whilst the pictures are washing in the water, and the whites will in consequence be discoloured. This may be obviated by washing them in weak salt and water, so as to decompose the remaining traces of Nitrate of Silver; but the proportion of Salt must not be greater than two or three grains to the ounce, or the image will become red and feeble. Ammonia would not be proper for washing, since it would at once discolour the Gallo-Nitrate.

The formula for a toning Bath may be taken from page 377, but it is questionable whether much Alkali ought to be used, since the Gallic Acid left in the paper would turn brown in presence of free Carbonate of Soda. Add, therefore, to each grain of Chloride of Gold not more than half a grain of the alkaline Carbonate. Avoid also a prolonged action of the toning Bath, since the tendency to a cold and inky colour is greater in developed Prints than in Sun-Prints.

Upon comparing the developed Prints with others obtained by the direct action of light, it is evident that the advantage is on the side of the latter; but the difference is not great, and would be overlooked in printing large subjects, for which the Negative process is more especially adapted. The colour of both kinds of Positives is the same, or perhaps a shade darker in the developed proofs, which are usually of a violet-purple tone, but sometimes of a dark chocolate-brown.

Failures.—Printing by development must not be attempted until the operator is quite conversant with the Negative process upon paper or Collodion. He will then be aware of the importance of excluding scattered rays of white light from the developing room, and of filtering all the liquids,—points which are not of so much importance in the ordinary mode of printing by direct action of light.

Citrate of Soda is used in the above process, and the difficulty of obtaining this Salt commercially is an objection. In making it extemporaneously by neutralizing Carbonate of Soda with Citric Acid, when Tartaric Acid is present as an adulteration, the Soda is in excess, Citric Acid having more neutralizing power than Tartaric Acid. Test papers would be of little use in examining the liquid, because Citrate of Soda itself has an alkaline reaction. It may, therefore, be desirable to notice the results which are likely to follow when the salting Bath contains free Carbonate of Soda. In the first place it would tend to dissolve the size from the paper, and to give the resulting Print a mealy appearance. Obviate the chance of this by not floating the papers longer than one minute. Secondly, Citrate papers with excess of Alkali remove by degrees the Acetic Acid from the exciting Bath, the effect of which would be at first to increase the rapidity of development and intensity of image; but afterwards, when the Bath became nearly neutral, to produce a foggy picture.

Experimenters in this process will do well to try the effect of varying the mode of development, by using the solution of Pyrogallic Acid and Citric Acid given at page 287, in place of Gallic Acid.

STEREOSCOPIC TRANSPARENCIES.

In some previous Editions the Writer described a mode of printing transparent pictures upon wet Collodion by placing a slip of card on the sensitive film so as to preserve an appreciable interval of separation between the Negative and the Collodion, and thus to prevent the latter from being soiled by contact with Nitrate of Silver. Many, however, who tried this plan met with only partial success, and hence the employment of one of the dry processes, given in the Fifth Chapter, is recommended in preference.

Negatives to be used in printing transparencies ought not to be very dense, otherwise there will be a danger of the shadows of the transparency losing depth by over-action of light, and presenting in consequence a pale translucent appearance. Sensitive films prepared by Russell's Tannin process, however, will bear an unusually strong light without solarizing, and hence Negatives may be printed by this mode, which from their excessive opacity would fail in producing a good transparency on a Fothergill plate. Negatives developed by Sulphate of Iron are often remarkably well adapted for producing transparencies.

Place the Negative and the prepared plate in contact, and squeeze them together in an ordinary pressure frame: not too strongly, however, or it will probably be found, after throwing off a few impressions, that the Negative has been scratched. Lay a strip of black velvet behind the sensitive film to absorb stray light.

The printing may be effected by an exposure of three or four minutes to gas-light, or of a few seconds to ordinary daylight. The subdued light of a room is very good for the purpose, and will probably form the latent image in about twenty seconds.

The development is more simple and easy than that o Camera-exposed pictures, on account of the strength o the light used in forming the latent image. Begin b cleansing the developing glass carefully, in order that th Pyrogallo-Nitrate may remain colourless for a sufficien length of time to bring out the image. This point is ver important. It happened on one occasion to the Writer, tha his experiments proved unsuccessful, and on looking abou for the cause, it was found at length to be due to a test glass used in developing. The only observable peculiarit about the glass was that it had a bluish tint when looke down upon, but the developer would not remain in it fo more than a minute without discolouring. Repeated attempts were made to cleanse the glass, but in vain; an after an ineffectual treatment with the strongest Nitro Sulphuric Acid it was set aside as useless.

Formula *No.* 2, of page 187, containing Pyrogallic Aci and Citric Acid, is perhaps better for developing transparencies than Gallic Acid: it gives a cleaner picture, wit less of the objectionable green tint. Moisten the surfac of the film with water, and apply the Pyrogallic Acid having previously mixed three fluid drachms of its solutio with ten minims of the 20-grain solution of Nitrate of Silver described at page 304. This will be found nearly sufficient to cover a stereoscopic plate. The image begins t appear in less than a minute, and is usually well out in fiv minutes. One portion of developer will often complete th action, if ten minims additional of Nitrate solution be adde towards the end. But usually discoloration of the liqui begins to occur before all the details are seen, and in tha case the film should be washed for an instant under a tap and the development recommenced with a fresh portion o Pyrogallo-Nitrate.

The pictures are fixed with plain Hyposulphite of Soda the solution being of the same strength as that used fo Negatives. They are then, after a careful washing of several minutes, lightly toned with a solution of Chloride o Gold containing a grain to ten ounces of water.

New Hyposulphite of Soda free from sulphuretting compounds, in fixing the image leaves it of a brown or yellowish tone, varying with the time of exposure and length of the development. A few drops of highly diluted Hydrosulphate of Ammonia (see the Vocabulary) will darken it considerably, and may be employed without fear of causing subsequent fading, since this image contains more real Silver than an Albumen sun-print (p. 53).

Remarks.—The foregoing directions for printing transparencies will by many be deemed insufficient, since the subject has excited interest in consequence of the extreme beauty of the results obtained by the Continental operators. The Writer confesses that he was until very recently unable to secure the rich sepia tone which is so greatly admired, and that his early Albumen pictures had too much of the yellow-green tint before toning, and of the inky coldness after toning. Latterly, however, he has obtained results which leave nothing to be desired, and this by simply following out Russell's Tannin process exactly as given in the Fifth Chapter. The Tannin imparts a strong brownish-red tone to the picture, which is not sufficiently corrected when the developer contains only Acetic Acid: Citric Acid in the developer modifies it, and gives the desired shade. Three points must be attended to in producing these transparencies. First, the Bromo-iodized Collodion must be kept for many weeks in the iodized state, or even for many months, if the Ether be pure, and the Pyroxyline stable. Old Collodion imparts a certain warmth and richness to the image which cannot be obtained with a newly iodized Collodion free from decomposition. Secondly, print by a light sufficiently strong to form the image in about twenty or thirty seconds, since it will be found that the colour of the picture varies with the intensity of the light by which it was printed. Thirdly, over-expose and under-develope as far as allowable, so as to favour warmth and redness. Observe that these prints require no toning: if the above precautions be attended to, they will reach the proper colour by simple development.

CHAPTER IV.

CLASSIFICATION OF CAUSES OF FAILURE IN THE COLLODION PROCESS.

SECTION I.—Imperfections in Collodion Photographs.
SECTION II.—Imperfections in Paper Positives.

SECTION I.

Imperfections in Negative and Positive Collodion Photographs.

FOGGING OF COLLODION PLATES.

1. *Over-exposure.*—The image in the Camera is rarely pure, but exhibits enough diffused light to produce universal clouding when the plate is at all over-exposed. Collodion newly iodized being more sensitive to a weak light, shows the fogging more than old coloured Collodion. When the objects are at a great distance, and brightly illuminated, or when Lenses of large aperture are employed, without a diaphragm, beginners are especially likely to over-expose the plates.

2. *Diffused Light.*—*a.* In the developing room. This is a frequent cause of fogging, and especially so when a naked candle is employed to illuminate, or the common yellow calico is used, which is apt to fade. Examine for cracks and crevices in the sides and floor of the room.—*b.* Mist in the atmosphere. When there is any vapour in

the air, the shadows will be foggy, unless the object be very near to the Camera.—*c*. Diffused light in the Camera: light may get in between the two portions of the body (p. 314).—*d*. Diffused light from the Lens. If a Portrait Lens, see how to protect it at p. 312. In the case of a View Lens producing a false glare of light, deal with it as described at p. 324. Orthoscopic Lenses sometimes give a foggy image from imperfect arrangement of the separate glasses, only to be corrected by the maker of the Lens.—*e*. Diffused light in instantaneous Photography. See page 354.

3. *Alkalinity of the Bath.*—This condition, explained at p. 132, may be suspected, if the operator has added Ammonia to neutralize Nitric Acid: in all probability he has used too much. If the Bath has been shaken up with Chalk or Carbonate of Soda to remove Nitric Acid, Acetic Acid must afterwards be used (p. 133).

4. *Acidity of the Bath.*—Too much Nitric Acid in a weak Bath will produce fogging (p. 47). Glass Positives are often cloudy from this cause.

5. *Organic Matter in the Bath.*—The Nitrate of Silver not freed from organic impurity by re-crystallization (p. 135), its solution decomposed by being kept in new Baths of Gutta-percha (p. 135), or by use of foul-smelling rain-water, or distilled water collected from condensed water of steam-boilers, and containing oily and empyreumatic matters. When a Bath gives foggy pictures from these causes, the longer the plates are left in it the worse will be the result.

6. *Use of colourless Collodion.*—Collodion iodized with Cadmium, and used within a week, or iodized with the Iodide of Potassium *and used immediately*, will often give foggy Negatives if the other solutions are not in the best working order. Mix the new Collodion with a little old Collodion, or drop in Alcoholic Tincture of Iodine until the Collodion becomes straw-yellow (p. 363).

7. *Heat of the Weather.*—If the Bath and Collodion are both pure, clear Negatives will be obtained at any

temperature short of 90° Fahrenheit. Above that point proceed to modify the developer as described at p. 164.

8. *Sulphate of Iron as a Developer.*—If fogging results, the Bath and Collodion give an insufficient amount of intensity (p. 165), or there is diffused light in quantity so small as not to be detected by Pyrogallic Acid, which is a less active reducing agent than Sulphate of Iron.

9. *Sundry other causes of fogging.*—*a.* Vapour of Ammonia or the products of the combustion of coal-gas, escaping into the developing room.—*b.* Development of the image by *immersion* in solution of Sulphate of Iron: it is better to pour the fluid over the plate, and not to use the same portion twice.—*c.* Redipping the plate in the Bath before development: this is apt to give a foggy picture when using an old Bath.—*d.* Omission of the Acetic Acid in the solution of Pyrogallic: this will produce a universal blackness (p. 47).—*e.* Developing solution inadvertently dropped into the Nitrate Bath.—*f.* Metallic Iron left in contact with the Bath solution.—*g.* Using too strong a developer in hot weather, or keeping any developer, and especially Sulphate of Iron, on the film for too long a time.

Systematic plan of proceeding to detect the cause of the fogging.—If the operator has had but little experience in the Collodion process, and is using Collodion of moderate sensitiveness and a new Bath, the probability is that the fogging is caused by *over-exposure.* Having obviated this, proceed to test the Bath; if it was made from pure materials, and does not restore the blue colour of a piece of litmus-paper previously reddened by holding it over the mouth of a Glacial Acetic Acid bottle (p. 133), it may be considered in working order; but in the case of an old Bath this does not apply, because the Bath may have been spoilt by organic matter.

Next prepare a sensitive plate, and after draining it for two or three minutes on blotting-paper, pour on the developer: wash, fix, and bring out to the light; if any mistiness is perceptible, either the developing room is not sufficiently dark, or the Bath was prepared with a bad sample of Nitrate of Silver, or with impure Alcohol, or impure water.

On the other hand, if the plate remains absolutely clear under these circumstances, *the cause of error may be in the Camera*;—therefore prepare another sensitive film, place it in the Camera, and proceed exactly as if taking a picture, with the exception of not removing the brass cap of the Lens: allow to remain for two or three minutes, and then remove and develope as usual.

If no indication of the cause of the fogging is thus obtained, there is every reason to suppose that it is due to vapour in the atmosphere, or to diffused light gaining entrance through the Lens.

For directions how to deal with a Nitrate Bath which has been made foggy by organic decomposition, see p. 137.

Foggy Negatives, if sufficiently intense, should not be rejected as useless: they may often be cleared by the application of a weak solution of Iodine, followed by a fixing Bath of Hyposulphite of Soda.

SPOTS UPON COLLODION PLATES.

1. *Newly iodized Collodion.*—*a.* Containing Bromide of Potassium in quantity more than the Collodion will dissolve: in this case the spots will be round and transparent, thickly studding the plate. Allow twenty-four hours to subside, and draw off the upper part.—*b.* The Collodion is free from undissolved particles of Iodide, but contains a fine sediment of Pyroxyline; specks from this cause are extremely minute and abundant. Three or four days' settling will clear the Collodion; but very often the specks will disappear, if a portion of a more intense Collodion be mixed with the newly iodized (p. 48).—*c.* The Collodion is free from suspended Iodide or undissolved Pyroxyline, but nevertheless the plate shows transparent specks. In this case, the specks may be due to dust, but the remedy last given is the most likely to be successful.

2. *Faults of the Bath.*—*a.* Newly made from impure

Nitrate of Silver (p. 135). In this case the image will be very weak as well as spotty, and the Bath will require a trace of Acetate, as described at page 410. The reason why a bath in this state produces spots is given at page 48.—*b*. Iodide of Silver previously dissolved in the Bath crystallizing upon the film. The film in such a case exhibits little projecting points upon the surface of the Iodide before exposure in the Camera, and transparent pinholes after fixing. Add to the Bath a sixth part of a thirty-grain solution of Nitrate of Silver, not containing any Iodide of Silver, and remove the plate from the solution after an immersion of two minutes. Or leave a sensitive plate in the solution all night, that the excess of Iodide of Silver may gradually crystallize upon its surface, and so be removed.—*c*. A floating film of Iodide of Silver upon the surface of the Bath. These spots are not universally distributed, and are larger than the last. Remedy: change the Collodion, or the time of dipping (p. 299).—*d*. Deposits of reduced Silver on the sides of the Bath and dipper or fragments of iodized Collodion which have fallen into the solution. Spots, so produced, are easily recognized, and the appearance of the picture at once shows that the Bath requires filtering.

3. *Dust as a cause of Spots.*—*a*. New apparatus is generally dusty, and the hinges full of brass-filings. Tents are the same, and so are dark boxes for working in the open air, or leather-bodied Cameras, especially when used for the first time in the season. Wipe them out with a damp cloth, but not immediately before working, if it can be avoided.—*b*. Hard rubbing of glasses in cleaning renders them electrical, and attracts dust. An electrical condition of glass tends also, as before shown (p. 51), to produce irregular action of the developer.—*c*. Dropping the plate suddenly into the slide, or tapping the slide against the ground, is likely to stir up dust.

4. *Faults of the Slide.*—Sometimes a small hole exists, which admits a pencil of light, and produces a spot, known by its being always in the same part of the plate; or the

door works tightly, so that small particles of French polish are scraped off, and projected against the plate when it is raised; or the operator, after the exposure is finished, shuts down the door with a jerk, and so causes a *splash* in the liquid which has drained down and accumulated in the groove below. The *hinges* of the slide also frequently produce a little row of white spots when brass-filings are left or dust accumulates.

In the experience of the Writer, spots upon the plate have been more frequently due to defects in the slide than to any other cause, and a simple rubbing with a piece of soap has often sufficed to remove them.

5. *Larger spots from concentration of the Nitrate of Silver.*—When the film becomes too dry after removal from the Bath, the solvent power of the Nitrate increases so much that it eats away the Iodide and produces transparent marks.

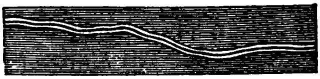
6. *Use of glasses improperly cleaned.*—After glasses have been long used, it is often difficult to clean them so thoroughly that the breath lies smoothly; spots due to this cause are of a large size, and always come in the same place.

Read the remarks at page 158 on the use of Bromide in preventing spots upon the plate.

MARKINGS OF VARIOUS KINDS.

1. *Transparent marks like Curtains.*—These occur at the edge of the plate which is most depending in the Camera, and are produced by the Bath solution draining down, or sometimes ascending by capillary attraction from the corners of a dirty slide. They are most common with a Gelatinous simply iodized Collodion, and are seen in cold and damp weather more than in hot and dry weather. To obviate their occurrence, allow the Ether to evaporate from the film before dipping, so that the Bath solution may run completely off; or turn the plate round, that the upper and drier part may be below; or place it across the dipper, so as to bring the curtain mark to the side of the picture, where it will be less visible.

2. *Wavy Streaks.*—Due to the Bath solution running into lines upon the surface of the film. The rivulet of liquid often acts like a Lens, and refracts the light which falls upon it in the Camera, producing an appearance like that shown in the woodcut.



Collodion of a tough and contractile structure, made with spirits comparatively anhydrous, and with an excess of Ether, favours these markings; a loose and powdery film showing them less frequently. Much however depends upon the Bath. Newly mixed Baths can be used successfully, but when Alcohol and Ether accumulate, and the Bath is slightly decomposed by organic matter, the marks appear in profusion. As a remedy, first try the effect of leaving the plate double the usual time in the Bath, and moving it several times up and down. Then drain with extra care on blotting-paper, especially so when the direction of the glass is to be changed on putting it into the slide; as for instance with stereoscopic plates, which nearly always show the marks on the picture which comes at the part lowest in draining. Supposing these plans to be insufficient, turn the plate round after coating it with Collodion, so as to bring the top downwards and to immerse the driest part of the film first in the Bath.

3. *Straight lines* like hairs, running in the direction of the dip in the Bath, are frequently observed when using a horny Collodion which sets rapidly upon the glass. The solution of Nitrate of Silver hangs about its surface, and either a lateral motion must be given to the plate immediately after putting it into the Bath (p. 300); or the Nitrate must be prevented from causing excess of reduction by using more acid in the developing solution.

When large black straight lines are abundant upon the film, the Bath is often in too reducible a state, being either alkaline, or loaded with Acetate of Silver. Frequently also the plate is under-exposed when such marks occur (p. 48).

4. *Structural crapy lines.*—Marks from glutinosity will sometimes occur when using Cadmium as an iodizing solution. A sample of plain Collodion which gives these markings, will probably be free from them after keeping for a few months, without any further treatment (p. 120). Structural lines on the film also frequently depend upon the plate not being properly rocked whilst pouring off the Collodion. Some operators dilute glutinous Collodion with Ether, but in doing so there is always a danger of precipitating the Iodide of Potassium, and if the Pyroxyline be of that kind which sets very rapidly, the use of too large a proportion of Ether will produce markings of a different kind, viz. such as are alluded to in paragraph 9 in the next page.

5. *A network appearance on the film after developing.*—When this is *universal,* and accompanied by rottenness of film, it often depends upon the employment of Collodion containing water. Or, if not due to this cause, the plate may have been immersed too quickly in the Bath, and the soluble Pyroxyline partially precipitated. This is very likely to happen when using Collodion containing a sufficient excess of Alcohol to interfere with the setting properties of the Pyroxyline (p. 299), especially in cold and damp weather.

6. *Oily Lines.*—*a.* Lifting the plate out of the Nitrate Bath before it has been immersed sufficiently long to be thoroughly wetted, or before the Ether upon the surface is washed away.—*b.* Redipping the plate in the Nitrate Bath after exposure in the Camera, and pouring on the developer *immediately;* if a few seconds be not allowed for the purpose of draining off the excess of Nitrate, the Pyrogallic Acid will not amalgamate readily with the film.—*c.* From too small a quantity of fluid having been employed to develope the image. In this case, the whole plate not being thoroughly covered during the development, the action does not proceed with regularity.—*d.* Opaque

oily diagonal markings are very commonly produced by pouring off the developer and examining the plate by transmitted light without washing the film: the solution of Pyrogallic Acid runs into lines which show after fixing.—*e.* Addition of old Collodion in making a new Bath. The Ether mixes with the Bath, and gives a greasy appearance to the immersed plates.

7. *Straight lines traversing the film horizontally.*—A check in immersing the plate in the Bath (p. 300).

8. *Curved lines of over-development.*—The developer too concentrated; or not poured on sufficiently quickly to cover the surface before the action begins.

9. *Marks like the woodcut* are exaggerated by holding the plate a long time before dipping it in the Bath. Excess of Ether in Collodion increases these markings, but dilution with Alcohol lessens them by preventing the rapid setting of the Collodion. The same Collodion which produces the marks when iodized with Iodide of Ammonium, and especially with Iodide of Ammonium containing free Ammonia, shows none when iodized partially or entirely with Iodide of Cadmium. Probably the difference depends upon the fact that Iodide of Cadmium thickens Collodion, whilst Iodide of Ammonium renders it limpid (p. 122). Chloroform in Collodion also modifies the structure, and a fluid sample of Collodion giving marks resembling vegetation, flashes of lightning, or watered silk, may often be cured by adding ten minims of Chloroform to each ounce, and allowing it to stand for twelve hours.

The marks can usually be seen upon the film by a close inspection after sensitizing, but if the Bath is pure and newly prepared, they will not invariably show in the development. With a Bath, however, which is prone to give foggy films and irregular reduction, they are exaggerated during development.

10. *Opaque yellow or white streaks at the part of the*

film from which the Collodion was poured off.—These, when seen upon the surface of the Iodide as it is lifted from the Bath, may depend upon the presence of too large a quantity of Iodide. In this case, the film appearing yellow and creamy, make a mixture of equal parts of highly rectified Alcohol and pure Ether, and slightly dilute the Collodion, or add a little plain Collodion to the iodized Collodion. Supposing these marks to appear, and the film to be rather opaline than creamy, add to each ounce a grain of Iodide of Cadmium (see p. 285).

11. *Thickenings of the Sensitive Iodide.*—These when visible on taking the plate out of the Bath, are often caused by pouring the Collodion from a full bottle, and holding it too high, so that the liquid spatters on the glass and produces air-bubbles, which course across the plate. Secondly, by employing a Collodion containing too little Alcohol: it cannot easily be applied to a large plate without leaving a band of thickening at one end. Try the effect of pouring less of the Collodion, so that the fluid shall not twice traverse the same part of the plate. Thirdly, thickenings are caused by fragments of dried Collodion accumulating in the neck of the bottle.

12. *Silver stains of varied shape upon the finished Picture.*—*a.* From altering the direction of the plate after removing it from the Bath, and placing the top edge downwards. This throws a wave of Nitrate back over the film, and often produces stains.—*b.* Scum upon the Bath. —*c.* Developer poured out of a dirty glass containing the scum of a previous reduction.

13. *A blue line at upper edge of film, seen on the Iodide before exposure.*—*a.* Often caused by using a Collodion made from highly rectified spirits, the Ether being in excess: the film in hot weather dries and shows iridescent tints at the upper part before it can be immersed in the Bath.—*b.* From use of too much Alcohol in Collodion, thus retarding the setting of the Collodion at the lower edge, to such an extent that the top part becomes dry.

14. *Transparent marks of various shapes, seen on the*

finished picture.—*a.* From wiping the glasses with a damp cloth.—*b.* From employing a thin Collodion very sensitive and neutral.

15. *Patches of a reddish colour by transmitted light on the shadows of the finished Negative.*—Try a second application of the Hyposulphite, which will clear them away if they consist of Iodide of Silver; but sometimes a deposit of this kind is due to irregular action of the developer, or to impurities on the glass (p. 344).

16. *The picture vanishes when the plate is fixed.*—In this case the Iodide was upon the film, and not *in* it. Pyroxyline made in acids weak enough to destroy the power of setting will produce this effect (p. 109); and the only remedy is to use more Ether and less Alcohol in dissolving such Pyroxyline.

17. *The picture survives the fixing, but disappears in the varnishing.*—Pyroxyline prepared in very weak acids is soluble in absolute Alcohol, and hence some varnishes will attack it. Change the varnish and all will go well.

18. *A scum left upon the surface of the Bath in dipping.* —*a.* Over-iodized Collodion.—*b.* Want of proper setting properties in the Pyroxyline; mix the Collodion with a sample of a different kind.

IMPERFECTIONS IN COLLODION NEGATIVES.

1. *The image weak and slaty-blue.*—*a.* Damp weather with the air full of moisture (p. 152).—*b.* The Nitrate Bath newly made from impure crystals (p. 135).—*c.* Excess of Nitric Acid in the Bath (p. 161).—*d.* Too much free Iodine in the Collodion (p. 132). In this case the colour of the Collodion will be nearly brown.—*e.* Bromide in the Collodion (p. 157).—*f.* Use of Sulphate of Iron as a developer (p. 165).—*g.* Camera-image very weak, as in copying old manuscripts, etc., of full size (p. 154).—*h.* Use of a Negative Collodion made from weak Pyroxyline (p. 114). —*i.* Sulphuric Acid left in the Pyroxyline from imperfect washing. In this case a piece of blue test-paper left in the plain Collodion one hour will show reddening at the edges.

—*k*. Coating large plates too leisurely, in hot weather: the film dries, and there is no penetration by the developer (p. 354).—*l*. Over-exposure. In the case of a bromo-iodized Collodion developed with Sulphate of Iron this is a common cause of feebleness of the image.

2. *The image black and white without half-tones.*—*a*. Under-exposure in the Camera (p. 306).—*b*. Yellow vapours in the atmosphere (p. 167).—*c*. The Nitrate Bath decomposed by long use, and containing organic matters injurious to sensitiveness (p. 136).—*d*. Collodion made at high temperatures, and kept after iodizing (pp. 115 and 158).—*e*. Non-actinic colours in the object to be copied (p. 341). *f*. Too rapid liberation of Iodine by Collodion (p. 319); especially when the film contains only a small portion of Iodide, and is semitransparent (p. 143).—*g*. Depression of temperature in the developing room (p. 166).—*h*. Impure Pyrogallic Acid. Bad samples sometimes develope the half-shadows imperfectly.

From whatever cause the above defect may arise, try the action of Sulphate of Iron as a developer: and give a longer exposure in the Camera.

3. *The image intensely red.*—*a*. The development not sufficiently pushed (p. 40).—*b*. The Collodion film under-iodized, and too transparent for Negatives.—*c*. Over-exposure in the Camera (p. 54).—*d*. Use of Collodion made from a highly intense kind of Pyroxyline (p. 115), and kept for some time in the plain state (p. 120): the redness is most marked when the Collodion is used newly iodized and colourless, since free Iodine tends to make the image blue.—*e*. Acetate in the Nitrate Bath (p. 162).—*f*. Alkalinity of the Nitrate Bath produced by shaking up with chalk, etc.—*g*. The light unusually brilliant, as in Photographing distant views and marine subjects.—*h*. The Camera image very bright, as in the case of short focus Lenses (p. 153).—*i*. Fixing with Cyanide of Potassium (p. 169).

When redness of the image is an objection, remedy it by use of Citric Acid in the developing solution, as described at page 164.

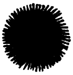
4. *Solarization of Negatives.*—Over-action of light ma produce either grey or red solarization (p. 50). In th former the image developes very slowly, and the shadow are wanting in detail. The plate shows no creaminess o looking down upon it, and the high lights instead of bein opaque are nearly or quite transparent, and bounded b dark outlines. The causes have been principally men tioned under the first heading in page 408.—*a.* Excess Iodine in Collodion, from keeping several weeks or month after iodizing.—*b.* Nitric Acid in the Bath.—*c.* Use of new Bath made from impure crystallized Nitrate of Silv (p. 135).

In *Red* solarization the plates develope rapidly, an often give a fair amount of detail in the shadows. Th superficial bloom is well marked, and the image brown b transmitted light; but the high lights are very pale an red, with a steel-blue tint by reflected light. The caus have been already indicated under the head of red Neg tives. They are,—*a.* Use of Pyroxyline made at hig temperatures, and kept for a long time in the plain stat but employed soon after iodizing.—*b.* Acetate in the Ba (p. 162).—*c.* Alkalinity of Bath.—*d.* Use of short-foc Lenses in a bright light. N.B. Collodion of that kin which produces red solarization when newly iodized, ofte gives grey solarization when kept until much Iodine eliminated; and a Nitrate Bath which solarizes red fro the presence of organic matter, may by keeping and add tion of Acid, be made to solarize grey, and produce Neg tives with reversed light and shade, such as are ofte termed transmitted Positives.

The proper remedy for grey solarization is the additio of Acetate to the Bath. Red solarization may be correcte by the use of Citric Acid in the developer (p. 164), or b the employment of Bromo-iodized Collodion.

Acetate may conveniently be added to the Bath in th form of crystallized Acetate of Soda, which can always b purchased. Dissolve three grains in a drachm of wate and pour the solution into twenty ounces of Bath; th white precipitate first formed will be taken up again on agitation. To prepare the Acetate extemporaneously, dissolve two grains of effervescing Sesquicarbonate of Soda in four minims of Glacial Acetic Acid, diluted with a drachm of Water.

5. *Blurring of the image.*—An irregular action of the developing fluid, giving an appearance as if the image had drained away to the bottom of the plate, often happens when some conditions are present which interfere with rapid and continuous development, such as,—*a.* The state of Bath described at page 135.—*b.* Bad light from presence of vapour in the atmosphere.—*c.* Weak Camera image.—*d.* Depression of temperature. As a remedy, try the effects of draining the plate more carefully before putting it into the slide; also, of halving the quantity of Acid in the developer, and doubling that of the Pyrogallic Acid; or, as a last resource, of adding Acetate to the Bath as above advised. N.B. Pyroxyline of the most sensitive but least intense kind, prepared by the use of weak acids, is especially liable to this defect when the other conditions are unfavourable.



6. *An opaque halo at the edges of the high lights.*—This defect is essentially different from that last described, and is caused by an excess of light. It may often be seen round the sky of a landscape Negative, or the windows of an interior. The less the intensity of the Collodion, the more marked the halo. Albumen in the film, in a dry process, exercises a favourable action, and tends to prevent the reduction of the Silver from extending beyond its proper bounds.

7. *Falling away of the film.*—This depends much upon the Collodion: the best kind for adhering tightly is that made in weak acids. When the Pyroxyline is not in a favourable state, the amount of Alcohol in the Collodion must be diminished (p. 117); but this observation does not

apply to a very hard and tough Collodion, because excess of Ether increases the contractility of such a film to so great an extent that it shrinks away from the edges of the plate. Any film, kept too long before dipping in the Bath, will slip from the glass at the upper part, and if dipped very quickly it is liable to peel away from below. Roughen the glasses at the surface as well as the edges (p. 291), and pour on the water for washing at the centre of the plate. Be careful that the fixing solution of Hyposulphite does not work underneath, and allow it to flow off at that corner which appears loosened. N.B. A very acid state of the Bath, and the use of Iodide of Cadmium as an iodizer, are both liable to cause gelatinization of the Collodion, and consequent slipping.

8. *The Collodion curls away from the glass on drying.*—This may occur with samples of Pyroxyline made in strong acids, especially when the Collodion is iodized with Cadmium. Also occasionally, when a very acid solution of Acetate of Iron is used in developing, or acid Bichloride of Mercury, or Chloride of Gold, applied to the film after it has become dry. Roughen the surface of the glasses (p. 291), and having coated the plate with Collodion and returned the excess into the bottle, draw the thumb along the lower edge of the glass to prevent the formation of a thickened band of Pyroxyline, which would be likely to split on drying. Do not immerse the plate in the Bath until the film has had time to set, and never employ imperfectly cleaned and greasy glasses.

9. *Woolliness in the skies.*—Employment of Pyroxyline made in strong acids with Cadmium as the iodizer. Try the mixed iodizer of Potassium and Cadmium, and substitute Alcohol of ·805 (see Part III.) for Alcohol of ·820.

10. *Turbidity of Developer.*—When the Pyrogallic Acid developer becomes muddy on touching the film, instead of assuming by degrees the colour of sherry wine, the Bath may be in fault. New Baths made from impure Nitrate of Silver will often produce the effect in a marked manner. Another cause is decomposition of the Pyrogallic Acid, by

keeping for several days in aqueous solution (p. 163). Also extreme heat of the weather. On the subject of dirty developing glasses, see page 396.

11. *Blueness of the Iodide Film.*—When a Collodion containing the proper quantity of Iodine produces an opalescent instead of a creamy film, an *organic impurity* is often present. Ether distilled from plain Collodion will often produce the effect, or Pyroxyline made at high temperatures, and kept for a time in solution. The Bath is sometimes in fault, organic matter having been introduced purposely or otherwise (see p. 137).

12. *Intensity of Image injured by Fixing.*—*a.* From the Collodion being too highly iodized. In this case the film will be dense and creamy, and will probably leave a scum on the surface of the Bath in dipping.—*b.* Insufficient development. The longer the action of the Pyrogallic Acid is continued, the less the chance of the image losing intensity in fixing.—*c.* Use of Cyanide of Potassium as a fixing agent (p. 169).

13. *Violet-Blue stains on Image after Drying.*—Hyposulphite of Soda left in the film in small quantity: the stains are mostly seen at the lower edge of the plate.

14. *Crystals on Image after Drying.*—Hyposulphite of Soda as before, but in larger quantity (p. 307).

15. *Difference of intensity on two halves of a Stereoscopic Plate.*—*a.* Old iodized brown Collodion of that kind which solarizes red when newly mixed, often produces this effect (p. 351).—*b.* Collodion prepared principally with Ether: it dries quickly in hot weather, and hence the second picture is less intense than the first.—*c.* In the case of dry Collodion plates developed with Gallic Acid, if the glass be not carefully levelled, the developer will accumulate at one end and produce excess of density.

16. *The developer flows in a greasy manner.*—*a.* From the Bath being old and containing much Ether and Alcohol. In this case a purely aqueous liquid is not suitable for amalgamating with the film, and a portion of spirit must be added to the developer (p. 288).—*b.* From use of too

much spirit in the developer when the Bath is newly made and nearly free from Alcohol : if the surface liquid of the film is entirely aqueous in character, the developer should be aqueous also.

17. *The developer refuses to wet certain parts of the film, and will not flow up to the edge.*—A gelatinous Collodion often repels the developer, and especially so with a newly prepared Bath. Old Baths containing Ether and Alcohol, render the surface of the film less gelatinous, and remedy the defect. The plate should not be dipped too quickly, or the difficulty will be increased. Acetic Acid and spirit added to the developer are serviceable. The stronger the Alcohol in the Collodion, the more marked the defect.

In hot weather, when large plates become partially dry, and repel the developer, redip them in the Bath, or use a developing solution greatly diluted with water (p. 168).

18. *The Collodion changes quickly after Iodizing.*—A rapid elimination of Iodine on adding Iodide of Potassium, may be due to the plain Collodion having been spoilt by exposure to light (p. 104), or to the use of Pyroxyline made at very high temperatures (p. 120): in this case, the longer the Collodion is kept in the plain state the worse it will become. Thirdly, to the employment of ozonized Ether, or of Pyroxyline left too long in the Nitro-Sulphuric Acid (p. 121). As a remedy, try the effect of iodizing the Collodion with Cadmium only, and keeping for a day or two. If this should fail, iodize with Iodide and Bromide of Ammonium (p. 284), and devélope with Sulphate of Iron. For directions how to bromize an old coloured Collodion, and thus to render it again useful, see page 278.

Discoloration of Collodion after iodizing, may also depend upon traces of acid left in the Pyroxyline from imperfect washing, but in this case the liberation of Iodine is slower than in the last, and may not be fully seen until the following day. Blue Litmus-paper left in the plain Collodion for six hours becomes red. Try as a remedy, agitation of the plain Collodion with powdered Chalk.

19. *An opalescent deposit limited exactly to those parts of the Negative which ought to be clear.*—This defect is due to a reversed action of the developer, and often indicates the existence of white light in the developing room. When such is not the case, consult page 344.

20. *Transparent lines enclosing diamond-shaped Spaces.*—Collodion made by the formula of page 262 will sometimes exhibit these markings, and especially when the Bath is not fully saturated with Iodide of Silver. Any Collodion will be liable to them when Glycyrrhizine is added to the Bath, or organic substances are present upon the surface of the film. Beyond re-saturating the Bath with Iodide of Silver, nothing can be done to remedy the defect.

IMPERFECTIONS IN COLLODION POSITIVES.

1. *The Shadows dark and heavy.*—The plate has not received sufficient exposure in the Camera; or the film being transparent and the Silver solution weak, too much Nitric Acid is present in the Bath; in the latter case, make the Collodion a little thicker, and develope with Sulphate of Iron containing only Acetic Acid (p. 280). Sometimes this defect depends upon the use of too little Bromide, the Collodion being decomposed by keeping after iodizing (p. 144): if so, increase the proportion of Bromide to a grain and a half per ounce.

2. *The Shadows good, the Lights vigorous but without detail.*—The developing fluid may have been kept on too long; or the object is too strongly illuminated (p. 311); or the Collodion is not adapted for Positives, giving a creamy film, and not containing much Bromide (p. 142).

3. *The high Lights pale and flat, the Shadows misty.*—The plate is over-exposed. Indistinctness caused by over-exposure is distinguished from that produced by fogging by holding the plate up to the light; in the former case the image shows as a Negative.

If the Collodion is colourless, clearer shadows will probably be obtained by dropping in Tincture of Iodine (ten grains to the ounce of Spirit), until a yellow colour is produced. But a still better plan will be to keep on hand a stock of old iodized Collodion for mixing with the newly-iodized. Too little attention is usually paid to the quality of the Nitrate of Silver for the Bath: this has much to do with clearness of shadow (p. 135).

4. *The picture developes slowly; spangles of metallic Silver are formed.*—Too much Nitric Acid is present in proportion to the strength of the Bath, to the amount of Iodide in the film, and to the quantity of Protosalt of Iron in the developer (p. 146).

5. *Circular Spots of a black colour after backing up with the varnish.*—These are often caused by pouring on the developer at one spot, so as to wash away the Nitrate of Silver; or by the use of glasses imperfectly cleaned.

6. *Silver Stains at the edges of the Plate.*—They often occur when using a forty-grain Bath strongly acidified. Pour on a large quantity of developer, so as to wash off some of the Nitrate of Silver into the sink, the stains being caused by excess of Nitrate.

7. *A green or blue Tint in certain parts of the Image.*—This is caused by the deposit of Silver being too scanty, which may happen from under-development, from too much exposure in the Camera, or from the film of Pyroxyline being *very thin;* if the Collodion be diluted down beyond a certain point, the same quantity of free Nitrate of Silver will not be retained upon the surface of the film. Add a few drops of the Bath to the developer before pouring it on the plate.

8. *Vertical Lines and Mistiness on the Image.*—If the Bath has been much used, add to it a third part of a simple solution of Nitrate of Silver in water, without any Alcohol or Iodide. Also prepare the developer with addition of Alcohol, to make it flow more readily (p. 288).

9. *Opacity of the Film on drying.*—Due to the use of Pyroxyline prepared in too weak acids (p. 144).

10. *Bad Colour of Image.*—The Pyroxyline too much of the Negative kind (p. 144). The Bath decomposed by use, and containing organic impurities.

SECTION II.

Imperfections in Paper Positives.

1. *The Print marbled and spotty on taking it out of the printing frame.*—The quality of the paper is often inferior, which causes it to imbibe liquids unevenly; or the amount of Silver in the Nitrate Bath is insufficient. In this case the spots are often absent at the lower and most depending part of the sheet, where the excess of liquid drains off.

2. *The Print marbled and spotty after toning but not before.*—*a.* Badly albuminized paper (p. 197).—*b.* The Print allowed to rise to the surface of the toning Bath. —*c.* Two or more Prints adhering, or touching each other so as to prevent the circulation of the toning liquid.

3. *The Print clean on the Surface, but spotted when held up to the Light.*—In this case the spots are probably due to imperfect fixation (p. 199).

4. *The Print has a cold and faded appearance when finished.*—*a.* The Chloride of Silver in the paper in excess with regard to the free Nitrate of Silver. This may be suspected when no *bronzing* can be obtained by prolonged action of the light, or when a weak solution of Nitrate of Silver was laid on with a brush, or by a glass rod (p. 182). Prints formed on paper which has been kept too long after sensitizing present the same appearance, the free Nitrate of Silver having entered into combination with the organic matter.—*b.* Over-action of the Gold Bath imparts a cold and grey tone to the picture.

5. *Yellowness of the light parts of the Proof.*—The following causes are likely to produce yellowness:—*Acidity* of the fixing Bath (p. 203); its action continued for too long a time; the first washings of the fixed proof not performed quickly; the fixing Bath laid aside until decomposed; the paper kept for several days after sensitizing,

6. *Intense bronzing of the deep shadows.*—Perhaps the Negative is in fault. Remedy it as far as possible by printing on paper containing but little salt; or sensitize the paper on a 30-grain solution of Nitrate of Silver instead of a 60-grain solution.

7. *The definition of the Print imperfect, the Negative being a good one.*—Much will depend upon the quality of the paper and the amount of Albumen used in preparing it (p. 180).

8. *Markings of a yellow tint in the dark portions of the Positive.*—Care should be taken not to handle the paper too much, either before or after sensitizing; to wash the prints in a clean vessel; and not to lay them down whilst wet on a wooden table, or in contact with anything likely to communicate impurities.

9. *Small specks and spots of different kinds.*—These, when not corresponding to similar marks upon the Negative, are usually due to metallic specks in the paper; or to minute insoluble particles in the Albumen which refuse to tone. Try the effect of halving the quantity of Carbonate of Soda in the toning Bath.

10. *Markings of the brush in Ammonio-Nitrate Pictures.*—In this case there is probably an excess of Ammonia, which dissolves the Chloride of Silver. Add a little fresh Nitrate of Silver, or use the Oxide of Silver dissolved in Nitrate of Ammonia (p. 376), and prepare the paper with only a small quantity of salt.

11. *Marbled stains on the surface of the sensitive Paper.*—Draw a strip of blotting-paper gently over the surface of the Nitrate Bath; and see that the sheet does not touch the bottom of the dish.

12. *Removal of the Albumen from the Paper during sensitizing, and white deposit in the sensitizing Bath.*—The Bath is probably alkaline, and contains too little Nitrate of Silver (p. 186). Add twenty grains of fresh Nitrate of Silver to each ounce, with a quarter of a minim of Glacial Acetic Acid.

13. *The Print refuses to tone.*—*a.* Often the fault of the

Albuminized paper.—*b*. Long keeping of the proof after printing (p. 198).—*c*. The toning Bath kept until it has become perfectly colourless (p. 195).—*d*. A trace of Hyposulphite of Soda carried from the fixing Bath into the toning Bath.

14. *Accidental over-printing.*—If the pictures when toned and fixed appear too dark, try Mr. Shadbolt's plan of agitating a pint of water with a minute quantity of liquid *Bromine* until it smells decidedly, and of then immersing the print until sufficiently reduced. Afterwards wash with water to remove the Bromine. This process eats away the print too much at the edges, but no better is known. Over-printed proofs may be reduced by toning in a Bath of Chloride of Gold from which the alkali has been omitted (p. 377).

15. *Skies printing through.*—This is often a fault of the Negative, and may be corrected as follows:—Dip a fine camel's-hair brush in Gamboge, and trace round the horizon of the Negative to about the sixteenth of an inch inwards on the defective sky. Then print an impression, and cut out the sky with a penknife. Blacken the paper sky by a proper exposure to light, and paste it on the Negative: the Gamboge tracing will prevent the line of junction from being seen. If the sky is defective only at the upper edge or at the corners, it will be sufficient to place a piece of brown paper in front of the printing frame, and to pack Cotton-wool beneath it.

16. *Difficulties in albuminizing paper.*—When the Albumen dries in streaks upon the paper, try the effect of adding two minims of Glacial Acetic Acid (previously diluted with a little water) to each egg; increasing the proportion of salt from ten to twelve grains per ounce, and that of the Nitrate of Silver in the Bath from sixty to eighty grains per ounce, if the addition of the acid be found to make the paper print too red, or to diminish the depth of the shadows to too great an extent.

CHAPTER V.

DRY COLLODION, AND COLLODIO-ALBUMEN PROCESSES.

Of the various methods alluded to in discussing the theory of dry Collodion in Part I., the Author selects *four* for more especial consideration. Being an advocate for the simplification of formulæ, he would have confined himself to a single process, had absolute certainty been obtainable. At present however this can scarcely be said to be the case, and hence it would be a mistake to limit the operator in his choice of resources.

Russell's Tannin process stands first upon the list, being the most closely allied to wet Collodion, both as regards the composition of the sensitive film and the quality of the picture. The experience of the Writer, as far as it has extended, is very much in favour of this method, but owing to its comparatively recent introduction, it has not as yet received a full trial. Fothergill's process is very simple, and enjoys a high degree of popularity: the Author himself, however, has not been uniformly successful with it, the Negatives being often solarized in the sky, and presenting other defects presently to be alluded to. Taupenot's Collodio-Albumen process is allowed by all to be valuable, although many are deterred from practising it by the labour involved in preparing the plates. In the case of long-focus Lenses, however, the process possesses so many advantages that no obstacle of the above kind ought to be considered. Lastly, the process of Messrs. Petschler and Mann may be recommended to such as desire to carry a large stock of plates with them on an excursion, and to leave all their baths at home. Bulky solutions of Nitrate of Silver are unpleasant companions on a journey, and are very liable to suffer injury before it is ended.

RUSSELL'S TANNIN PROCESS.

A newly iodized Collodion will succeed in this process, since the Tannin has an extraordinary effect in increasing the intensity. Nevertheless the picture, although sometimes requiring a longer exposure, will be more brilliant when an old iodized Collodion is employed in preference. The normal Collodion of page 262 bromo-iodized in the manner described at page 284 has been found successful, and when pure Ether is employed, this Collodion will remain in perfect working order for six months after iodizing. At first it is scarcely as porous as could be desired, but acquires this condition by degrees under the influence of the alkaline iodide. A Collodion of a more spongy character would be superior when newly iodized, but it would scarcely bear the same length of keeping, because as the film became by degrees powdery and rotten, the sensitiveness to dark shadows would be injured.

In this process the tendency to blistering of the film is not seen, but the Collodion will sometimes wrinkle and peel away from the glass at the lower edge. No preliminary coating to the glass will be required when the Collodion is in the most suitable state for adhering tightly, and when the glasses are small. Glasses of 10 × 8 and upwards will require the use of Gelatine, and even Stereoscopic glasses must be coated with it when the Collodion shows a tendency to separate, or if the operator should fail to observe the directions given for ensuring adhesion.

Clean the surface of the glass with great care, and for that purpose use a liquid capable of removing grease, such as the Tripoli mixture of page 291, or the old Collodion described at page 292. The glasses must be *quite dry* at the time of coating with Collodion; and hence if the room is damp and cold a fire must be lighted. When the Gelatine solution is used, the above precautions are less needful, but even in that case a greasy plate would probably cause slipping of the film.

The formula for the Gelatine liquid is as follows:—Nelson's patent Gelatine, 20 grains. Distilled water, 10 fluid ounces. Dissolve, filter through blotting-paper, and add half an ounce of Alcohol of ordinary strength to prevent decomposition by keeping. No gelatinization occurs on cooling, and the solution ought to remain good for a very long time; the Writer has used it after six months, but the test of smell will be reliable. Isinglass gelatinizes more firmly than common Gelatine, and a grain to the ounce of water will often give a viscidity about equal to that of iodized Collodion. The film left on evaporation is excessively thin, but it answers the purpose of fixing the Collodion better than a thicker film.

The application of the Gelatine solution to the glass is more troublesome than that of the Collodion, since it flows with difficulty, and if the glass be at all greasy, will not readily wet it. Pour a large pool of the aqueous liquid on to the centre of the plate, and if it does not run, guide it with the finger or a glass rod, taking care to keep the back of the glass clean. Allow the excess to flow back into the bottle, and when particles of fluff are seen floating, filter it through blotting-paper before using it a second time. Rear the plates on end to dry, with blotting-paper beneath, and when they are well drained, draw a slip of blotting-paper along the lower edge, to remove an accumulation of the gelatinous liquid. This precaution is quite necessary, since it will be found that if too thick a film of Gelatine be left on evaporation, the film will remain perfectly transparent on passing through the Nitrate Bath (p. 231), and no image will be developed on applying the Pyrogallic Acid. The plates should be dried spontaneously in a place free from dust, and if the attempt be made to dry them hurriedly, the Gelatine solution will often collect into ridges, and will leave a series of transparent marks on the surface of the excited Collodion as above described. This irregular drying almost invariably occurs in the case of a gelatinous liquid, but the Writer has seen glasses coated with diluted Albumen, and dried at a fire, without any such inequalities being produced. When the coated plates are surface-dry, warm them gently, and put them away in a grooved box, where they will remain good for a long time. Before packing them, however, it will be desirable to examine the back of each glass, and cleanse it from any adhering Gelatine, which, if allowed to remain, would affect the Nitrate Bath injuriously (p. 136).

Coat with Collodion exactly as usual: the presence or absence of the Gelatine film will scarcely be noticed. Allow the full length of time to elapse before dipping, otherwise the Collodion will certainly lie loose at the lower corner. Beginners frequently fall into the opposite error, and produce plates which are pale and opalescent, with a blue line running round the upper edge. The proper rule to follow is to touch the lower corner of the film with the finger after it has ceased to drip, and thus to ascertain how much setting power the Collodion possesses. If the Gelatine was applied as a preliminary coating, be very careful to cover *the whole plate* with Collodion.

The Nitrate Bath is an ordinary 30-grain solution, tested and found to be in working order for the wet process. Many will use a stronger Bath by preference, and in preparing the solution purposely, it is perhaps as well to make it of 35 or 40 grains to the ounce. The *immersion* ought to be longer than that often adopted for wet Collodion: from three to five minutes being an average time.

Lift the sensitive plate from the Bath, and without any previous wiping or draining on blotting-paper, wash it freely under a tap for about a minute: or place the plate in a tray of common water, face upwards, and after waving the water backwards and forwards for a few seconds, leave it until a second plate has been coated with Collodion and immersed in the Nitrate Bath. Then return, and continue the washing in the first water until all greasiness of the surface has disappeared, when the plate may be washed for a corresponding time in a second. Bath of common Water, a few drachms of Distilled Water being applied finally, if the common Water is very hard.

After the plates have been washed, the Author has frequently poured a solution of Salt over the film (five grains to the ounce of Water), and then washed them a second time under the tap. This proceeding undoubtedly lessens the sensitiveness to dark shadows, and diminishes the rapidity and redness of development, but it increases the keeping qualities. The principal danger to be apprehended when no salt is employed, is that traces of the image will appear upon the plate before development, and that the action of the reducing agent will be uncontrollable. In cool weather, and with recently prepared plates from old iodized Collodion, no such effect will be perceived, and in that case the quality of the Negative will be better without the Salt than with it; especially when the Lens has a long focus.

The preservative solution is prepared by the following formula:—

Tannin	15 grains.
Distilled Water . . .	1 fluid ounce.

Any druggist will supply Tannin, and it dissolves in the water almost as readily as Pyrogallic Acid. The solution is slightly opaline, but it runs through blotting-paper immediately, thus contrasting favourably with glutinous liquids like Gum or Albumen. Mould forms in the liquid after a time, but not so rapidly as in a solution of Gallic Acid. A sixth part of Alcohol replacing Water in the formula assists in its preservation, but the trouble of preparing it is so small, that decomposition by keeping becomes of little consequence.

Measure out two separate portions of the Tannin solution, containing, for a Stereoscopic plate, about two fluid drachms each. Apply the first two or three times to the washed film to remove the adherent water; then pour the second portion on and off, and rear up the plate to dry on blotting-paper in an absolutely dark place. Finish by artificial heat (p. 430), since the image is apt to be blurred and ill-defined when the plates are not perfectly dry.

If the glasses were not coated with Gelatine before the Collodion, the chance of wrinkling and contraction will be much lessened by dipping a camel's-hair brush in any quickly-drying Negative Varnish, and running it round the edge of the film, to about an eighth of an inch inwards on the surface. For Stereoscopic plates this plan will usually be sufficient to fix the Collodion.

Directions as to time of exposure will be found under the head of Fothergill Process, and Taupenot Process. The method now under consideration is, according to the experience of the Writer, more sensitive than an Albumen process by at least one-third, but the Citric Acid in the developer, although improving the colour, appears to add something to the required exposure, and since a powdery structure of the Collodion film has the same effect, the directions given under the head of the Collodio-Albumen method may be adhered to.

Develope as soon as possible: the Writer has had no experience with plates kept longer than six hours after exposure. The evening of the same day is convenient for this part of the process.

The developer is made from the two following solutions:

No. 1.	Pyrogallic Acid	72 grains.
	Alcohol	1 fluid ounce.

Dissolve, without filtering, unless there be evident turbidity. The solution ought theoretically to keep for months without much change, but the Writer is unable to speak from actual experience.

No. 2.	Nitrate of Silver	20 grains.
	Citric Acid	20 grains.
	Distilled Water	1 fluid ounce.

No filtering needed unless a white precipitate of Citrate of Silver should fall; as will sometimes be the case when the Nitrate of Silver was previously fused. The keeping properties of this solution are not remarkable, a warty substance of unknown composition sometimes forming: the supernatant liquid however appears to retain its action (?).

Begin by diluting thirty minims of No. 1 with three ounces of Distilled Water: the resulting solution will keep for twenty-four hours, but eventually turns yellow from absorption of Oxygen. Next place the diluted liquid upon the table side by side with the concentrated Alcoholic solution, and all will be ready for the development.

To develope, first moisten the exposed plate with water; not necessarily distilled water, but as free as may be from saline impurities. Do this evenly and quickly, or there will be curved lines in developing. Now, for a stereoscopic plate, measure out three drachms of the diluted No. 1, and add to it from 10 to 20 minims of No. 2. Apply this mixed developer, and keep it gently moving on the plate. Allow it to act for a short time, and watch the process of the reduction. If the sky developes strongly, but is not gradually followed by the darker portions of the object, the plate was under-exposed, and the picture will then be harsh, unless the developer be immediately strengthened by pouring it back into the measure, and adding 10 additional minims of No. 1 to the three drachms, so as to raise the proportion of Pyrogallic Acid to four or five grains to the ounce. If on the other hand the whole image appears simultaneously, add a few more drops of the solution No. 2, in order to increase the opacity of the sky. The theory of this part of the process will be found fully described at page 228 of the First Part of the work.

The ordinary solution of Pyrogallic Acid and Acetic Acid employed in the wet process (p. 287) may be used in this dry method. If however the plates appear too red, and exhibit a tendency to fogging on the shadows, the use of the Salt Bath of page 424 must be adopted, in order to destroy the last portion of Nitrate of Silver by conversion into Chloride of Silver.

Observe that in Russell's Tannin process the porosity of the Collodion is very little maintained, the preservative solution being thin and limpid. Hence these plates would certainly develope slowly, were it not for the reducing properties of the Tannin. Those who desire to prepare their plates in such a way that the film will expand on being wetted, are advised to mix Gum Arabic with the Tannin, taking from 15 to 30 grains of Gum to the ounce of Water.

The image having been developed to the proper point, fix the plate with solution of Hyposulphite of Soda, and varnish in the usual way.

FOTHERGILL'S DRY PROCESS.

This process is more dependent upon the state of the Collodion than that last described, and unless a certain amount of porosity co-exist with the organic reactions which are necessary to intensity, the developed image will often be feeble. The normal Collodion of page 262, even when Bromo-iodized, is not so suitable for Fothergill's process as some other kinds, being too dense in structure, and too feeble in developing unless after a long keeping in the iodized state. Although very tolerable pictures have been obtained with this Normal Collodion, yet the formula of page 342 affords better promise of success, the contrast of image being greater, and the film less liable to solarize. A little decomposition brought about by keeping the Collodion, is an assistance; Fothergill pictures of a satisfactory quality have been taken with Collodions which by transit to distant parts of the world had become too rotten and insensitive for the wet process.

The glasses will scarcely require any preliminary coating of Gelatine or Albumen as described at page 422, unless they are of a large size. It will be sufficient to clean them carefully with old Collodion or Tripoli, and to see that no moisture is present at the time of applying the Collodion. The directions for coating and dipping in the Bath already given under the head of "Russell's Process," page 423, will apply also in this method, and the strength of the Bath may be the same, viz. from 30 to 40 grains to the ounce of Water.

Mode of washing the Film.—This, as already shown when explaining the theory in Part I., is the most important part of the process, and the one on which success or failure mainly depends. A small quantity of Nitrate of Silver must always be left for the purpose of coagulating the Albumen and combining with it; and when the Collodion is deficient in those qualities which give intensity to the development, a still larger quantity of Nitrate of Silver will be required to fix the Albumen abundantly upon the film, and thus to secure the desired effect. Further than this it has been shown* that the same quantity of water applied to two Collodion films differing in physical structure will often cleanse one more perfectly than the other. Therefore no universally applicable rule can be given, but the Photographer will act wisely in inquiring of the maker of the Collodion the extent of washing which he recommends previous to albuminizing.

When a Collodion which ought to be washed very slightly before albuminizing, is thoroughly washed, the image developes slowly, exhibits no red translucency at the early stage of the development, usually fogs more or less, and is wanting in contrast. When on the other hand a Collodion requiring considerable washing, is not much washed, the image developes rapidly, shows a red tone at first, and is strong in contrast. Defects however soon arise, such as markings of varied form due to a clotty coagulation of the Albumen, and perhaps *fogging* from incipient reduction of the Albuminate of Silver. The more the plates are washed, the longer they will keep in the sensitive condition, and hence the washing should always be carried as far as possible without sacrificing the contrast of the Negative.

The Author, in his own practice, has not been able to exceed the four fluid drachms of water advocated by Mr. Keene, of Leamington, as the correct quantity for a Stereoscopic plate. But others, using a different Collodion, have placed their plates in a tray of distilled water, and washed them gently until greasiness disappeared. This latter plan is certainly more convenient, when it answers, since there are few who on first commencing the art can manipulate with sufficient dexterity to wash a plate evenly with a limited quantity of water; and when the washing is uneven, there are always markings from partial coagulation of the Albumen.

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* Ackland's 'Hints on Fothergill's Process,' published by Messrs. Horne and Thornthwaite, Newgate Street, London.

Supposing the four-drachm method to be adopted, proceed as follows:—After removing the Stereoscopic plate from the Nitrate Bath, stand it vertically on blotting-paper, and allow it to drain as long as would be required for a wet plate, wiping the back meanwhile in the usual manner. Then take it in the left hand, either by one corner or with the pneumatic holder, and having arranged the yellow light so that it falls nicely upon the surface of the film, hold it quite level, and pour on the half-ounce of water, waving it backwards and forwards. It should not be poured on entirely at one spot, or too much of the Nitrate of Silver would be displaced, producing a circular mark of imperfect development. As however a vacant space of a quarter of an inch in breadth is usually allowed at each end of a stereoscopic plate, this will be found convenient for pouring on the water, which must be allowed to run into each corner until greasiness has disappeared. It will probably touch the fingers by which the plate is held, and when they are not scrupulously clean, stains will in consequence result. After pouring away the water (which ought then to measure at least *three drachms* if the operation was well performed), drain the plate for an instant, and it will be ready for the Albumen.

Observe the importance of using either distilled or pure rain-water for the above washing. If Chlorides or Carbonates are present *to any considerable extent*, as is usually the case in hard water, they will decompose the Nitrate of Silver, and cause a milkiness.

The Albumen solution.—Take the white of a fresh egg, and add to it an ounce of distilled water, with three drops of strong Ammonia. The Ammonia preserves the Albumen from becoming sour and mouldy, makes it run more easily through the filter, and slightly increases the intensity of development. The solution will usually keep for several weeks.

Shake for ten minutes in a bottle, and pour out the liquid on a filter previously wetted. If the paper is sufficiently thin (Papier Joseph), the liquid ought to pass through drop by drop; but as eggs vary in glutinosity, there may be a difficulty, and in this case more water must be added, or fine muslin substituted for paper.

Apply the filtered Albumen twice or thrice to the film in the same manner as Collodion. Then pour water over the plate for a minute, in order to remove the excess of Albumen, and afterwards rear the glass on end to drain upon blotting-paper. The second washing may be done with ordinary water, but if Lime Salts are present in quantity sufficient to make a decided milkiness with Nitrate of Silver, it will be a safe precaution to finish with a few drachms of distilled water.

The propriety of adding common salt, or Phosphate of Soda, to the Albumen in the Fothergill process, has been lately discussed, and an increase both of sensitiveness and intensity has been attributed to their use. On trying the experiment, the Writer did not succeed in obtaining any marked advantage, and therefore he prefers to leave the formula as he found it. If the solution of Salt were used, it would probably be better to apply it *after* the Albumen, and thus to increase the keeping properties of the plates? but a slight diminution of contrast and intensity might be expected to follow its employment as a final bath.

When the plates are perfectly dry, they are ready for exposure, but as the sensitiveness is lessened by adhering moisture, it is recommended to use artificial heat in damp weather. Warm the contained air of a deal box, by means of a common flat iron, and stand the glasses at the sides after removing the iron. The plates may be placed in a box of this kind whilst still wet, and the moisture steamed off by artificial heat; but this is a hazardous plan, and it will be better to get them surface-dry before using the iron.

Exposure.—The sensitiveness has been stated to be double that of the Taupenot process; but the pictures shown to the Writer in corroboration were more or less imperfect in the shadows, and he believes that a gain *of one-third* is nearer the mark. From two to four minutes may be allowed on a favourable day, according to the distance of the view, and the amount of foliage; or from five to ten minutes in a dull light. The above exposures are for a stereoscopic Camera mounted with a single lens: further particulars are given in Taupenot's process, page 437.

Development.—This process is not quick as regards development. When a full quantity of Nitrate of Silver is left upon the film before applying the Albumen, it will be somewhat more rapid, but as a rule, two of Russell's Tannin plates may be developed to one of Fothergill's; the same reducing agent being employed in each case. Theory teaches us to expect a slow development in Fothergill's process, because the porosity of the Collodion is not well maintained by the preservative (p. 220); and in addition to this it can be shown that the employment of *Albumen* always diminishes the rapidity of development, although it increases the intensity.

The advocates of the Fothergill process mostly recommend the ordinary formula of Pyrogallic Acid and Acetic Acid (p. 287), but for Stereoscopic transparencies the Writer prefers the second formula of the same page, viz. Pyrogallic Acid and Citric Acid, which preserves the clearness of the shadows: the *Alcohol* in the formula must be omitted. The use of Gallic Acid for dry plates is also much to be recommended, the Negatives being developed face downwards, upon a solution of Gallic Acid, in the manner described at p. 439.

When Pyrogallic Acid is used, each drachm of the liquid is previously mixed with about five minims of a solution of Nitrate of Silver containing twenty grains to the ounce of Water. The film is first wetted, and the mixed developer poured on and off from a glass measure. This measure must be scrupulously clean, or defects will result,

which are described at page 412. In two or three mini
the developing solution may turn brown, and if so, a
cond portion must be used to complete the reducti
From five to ten minutes will be occupied in bringing t
Negative up to the proper point.

Fixing.—Hyposulphite of Soda is better than Cya
in all cases where albumen is employed, as being less lik
to dissolve the delicate details of the Negative.

Failures.—Those which the Writer has met with h
depended either upon the plate being held at the corn
by dirty fingers, or upon the use of newly iodized Co
dion too copiously washed before putting on the Album
In the latter case everything goes wrong, and there
spots, stains, and marbled markings, such as would
occur if the particles of Iodide had been in the state to
ceive a decided impression in the Camera (p. 48).

Markings like those on watered silk are also a comm
cause of failure; they probably depend partly upon
structure of the Collodion, but are exaggerated by the
of Albumen fully coagulated by excess of Nitrate of Sil
The remedy suggested is to keep the Collodion for a lon
time in the iodized state, or to mix it with another sam
which is free from the markings. The remarks made
page 406, failure No. 8, may also be studied with adv
tage.

TAUPENOT'S COLLODIO-ALBUMEN PROCESS.

Cleaning the Glasses.—This part of the process must
conducted with care, since the Albumen which is laid u
the Collodion, tends to raise the latter in blisters:
mode of obviating which is to clean the glasses in suc
way that the film adheres with tenacity.

Old Collodion may be used for cleaning, or in place
it the mixture of Tripoli powder and Ammonia descrit
at page 291.

The Collodion.—All necessary information on Collodi
will be found in the Ninth Chapter of the First Part of
Work. One great advantage of this process in fact c

sists in its being comparatively independent of the Collodion. Blistering of the film during development is the principal matter which requires attention, and for this a suitable Collodion is the most available remedy. Old Collodion, iodized with alkaline Iodides, and which has become short and porous in structure by gradual decomposition, is the best kind to employ; but it will frequently happen on attempting to coat the plate with such Collodion, that it proves to be too limpid, and leaves an uneven coating upon the glass, thicker below than above. In such a case a grain and a half of Iodide of Cadmium to the ounce will often thicken it sufficiently; if not, a little newly iodized Collodion must be mixed with it, or two grains of Pyroxyline dissolved in each ounce. The normal Collodion of page 262 will usually require this treatment after six months' keeping, but in other respects it is peculiarly well adapted for Taupenot's process, since the large excess of Sulphuric Acid, and of water, employed in the formula for the Nitro-Sulphuric Acid, are both highly favourable to adhesiveness of Collodion.

Sensitizing and Washing.—It is usual to employ two Nitrate Baths in this process, one for the Collodion, and the other for the second film, viz. the Albumen. The Albumen Nitrate Bath must contain free Acetic Acid, and therefore if one solution be employed for both films it should be a Bath of Aceto-Nitrate. Very good results have been obtained with a single Bath, and it is more convenient in travelling; but it has always appeared to the Writer that the Collodion sticks better to the glass when sensitized in a clean and neutral Bath, and therefore when portability is not an object, he advises to keep the Baths distinct.

Sensitize the Collodion in the ordinary way, holding it rather longer than usual before dipping, to favour perfect adhesion and so to prevent blistering. Then having arranged two dishes of common water side by side, lay the plate face uppermost in the first dish, and wave the water backwards and forwards for about thirty seconds. Then put the plate into the second dish and leave it whilst another glass is being coated and immersed in the sensitizing Bath. Now drain plate No. 1 closely on blotting-paper, and it will be ready for the iodized Albumen. Plate No. 2 remains in the sensitizing Bath until the first glass has been coated with Albumen and placed to dry.

Preparation of the iodized Albumen.—Procure eggs fresh laid, or not more than a week old. The fact of the decomposition of Albumen being attended with a liberation of *Sulphur* will be enough to put the operator upon his guard against stale eggs, since the deleterious effects of the Sulphur compounds in Photography are well known. Take of

Albumen	3 fluid ounces.
Distilled Water	1 fluid ounce.
Strong Ammonia	10 minims.
Iodide of Potassium . . .	10 grains.
Bromide of Ammonium . .	10 grains.

First mix the Ammonia and the Water, then add the other ingredients, and shake together in a bottle. This mode of proceeding will be found more fully described under the head of Albuminized Paper (p. 369).

In preparing the Albumen solution it must be borne in mind that the viscidity of different eggs varies: hence it will be occasionally necessary to introduce a little more Water, in order to make the liquid run through the filter. The filtering paper ought not to be as close in texture as Swedish filtering paper, but Papier Joseph will usually answer. Some operators filter through a piece of sponge, but the difficulty is to push the sponge down with sufficient firmness to stop back floating particles without choking the neck of the funnel: a piece of fine cambric appears to the Writer to be better, but he prefers paper when the Albumen can be made to run through it. After Albumen has once been filtered it will run more easily a second time, and it will also flow better after a few days' keeping, since the Ammonia gradually liquefies it, and removes much of the glutinosity.

Instead of Iodide of Potassium, Iodide of Ammonium may advantageously be used when it can be obtained pure, being a more soluble salt, and thus less likely to cause pinholes in the Negative by crystallizing in the Albumen. Iodide and Bromide of *Cadmium* cannot be used, since they have the property of coagulating Albumen.

Another addition is sometimes made to the Albumen solution, viz. common white Sugar, in the proportion of one drachm to each ounce of Albumen. It must be added after filtration, as it increases the viscidity. The use of the Sugar is to lessen the chance of the blisters before referred to, by mechanically altering the Albumen. Nitrate of Magnesia and other deliquescent Salts have been employed with success for a similar purpose.

The keeping properties of the prepared Albumen vary. It will often remain good for a month, if a piece of Camphor the size of a pea be left floating on the surface; but sometimes mucous threads form, or a white deposit falls, which must be filtered out.

To apply the Albumen.—For a glass of Stereoscopic size measure out one drachm of the Albumen and pour it on and off twice, to displace the surface water of the washed Collodion film. Then throw it down the sink, and apply a second quantity, which will serve as the preliminary portion for the succeeding plate. The stock of Albumen is thus kept pure and undiluted.

Stand the Albuminized plates vertically on blotting-paper to drain and dry. The process, when nearly complete, may be hastened by artificial heat (p. 430), or the plates may be dried off at once, whilst still wet.

Collodio-Albumen plates ought, on theoretical grounds, to admit of being prepared thus far in open daylight, since the Iodide of Potassium would obliterate any actinic effect previously produced upon the Collodion surface (p. 231). Some however who have tried the experiment of exposing the plates to strong sunlight in the first stage, have found that the action was not entirely removed by the subsequent use of Iodide: the state of the Collodion and the quantity of free Nitrate of Silver left upon the plate would probably influence this point.

The Aceto-Nitrate Bath.—Take an ordinary Collodion Negative Bath, and add to each fluid ounce thirty minims of Glacial Acetic Acid; keep it in glass or gutta-percha, and continue to use it until it has become blackened by the action of the Albumen (p. 373). Then decolorize by Kaolin in the usual way. It may require some weeks or months to bring the solution to the colour of claret, and the Writer has printed transparencies quite clean with a Bath of this kind, so that it is a mistake to purify it too frequently. An occasional filtration or cleansing of scum from the surface will be required.

Complaints have sometimes been made that the Aceto-Nitrate Bath loses all its Acid after a time, and produces foggy pictures. Albumen is an alkaline substance, and will render a neutral solution of Nitrate of Silver alkaline by degrees (p. 188): but a portion of the Acetic Acid undoubtedly disappears in the form of Acetic Ether. Old Collodion Baths contain abundance of Alcohol, and when they are converted into Aceto-Nitrate, the characteristic sweet smell of Acetic Ether soon becomes perceptible. The film of Albumen must be rendered quite dry by holding it to the fire before it is dipped in the Aceto-Nitrate Bath. All agree that blisters are less frequent, both when the glasses are well dried before putting on the Collodion, and again after coating with Albumen. Leave them in the Bath any time from thirty seconds to two minutes, and then remove and wash with water.

Use two dishes for this washing, and allow twenty or thirty seconds in each dish; then rear up again to dry, and the plates will be ready for exposure. Artificial heat may be used with advantage as before; a common flat-iron being placed in the centre of a box and the glasses arranged at the sides. If little blisters appear on the surface of the Albumen when it is half wet and half dry, they will probably come out with increased strength in the development.

Exposure in the Camera.—Carry the plates in a grooved tin box, or a box of mahogany. Pine or deal is not recommended, on account of the volatile resin it contains, but a box of this kind may answer when no better can be obtained. Change the plates after exposure by means of a large bag made of two thicknesses of yellow and one of black calico, with a window cut out of the latter at the side, and an elastic band to draw round the waist.

Dry-plate Cameras are made purposely, very portable; also dark-boxes for sliding the glasses backwards and forwards as required. The objection to the dark-box is, that unless the glasses are cut with unusual care, they will not always slip readily, and the Writer prefers either the black bag above described, or separate backs for the Camera, each enclosing a prepared plate.

The most successful operators in Taupenot's process give a very long exposure, which has the effect of softening the picture, and obviating that excessive contrast or hardness which is often complained of in Albumen Negatives. The chances of fogging in development, however, are increased by lengthened exposure, when the film is not in very good order, or more especially when the Camera admits any diffused light. Three minutes may be mentioned as an average time for a Stereoscopic view in a good light, eight minutes for a picture on a plate 10×8 under the same circumstances, or twenty minutes for a group of trees rather near to the Camera, the Lens being of fifteen-inch focus, and half-inch diaphragm. When the film does not solarize very readily, five minutes may be given to one-half of a Stereoscopic plate, and ten minutes to the other, when a slight excess of half-tone in the latter will be the only observable difference on developing. In other instances, however, where from hardness of washing water, etc., over-action of light is encouraged, the skies will be nearly free from deposited silver, if too much time be allowed in the Camera.

Development.—Prepare a saturated solution of Gallic Acid in distilled water, adding four grains to each ounce.

Rain water, when containing traces of Ammonia (see Vocabulary, Art. "Water"), and spring water contaminated with Chalk, are both useless for this solution, since any alkalinity causes the Gallic Acid to discolour on adding the Nitrate of Silver. Gallic Acid is not immediately soluble in water like Pyrogallic Acid, and artificial heat will be required to dissolve the full quantity. It is a common plan to put a decided excess of the crystals into a bottle, and shake them up for several hours in cold water; after which the solution may be considered to contain from three to three and a half grains of Gallic Acid per ounce. Always filter this developer through paper, since in a dry process little floating particles would be more likely to cause spots than in the case of wet Collodion.

Solution of Gallic Acid becomes mouldy on keeping. To restrain this tendency drop in two or three small lumps of Camphor, and leave them floating in the liquid. The quantity of Camphor dissolved is very small, but enough to give a decided smell and taste. It is of still more importance not to put the solution into a dirty bottle. If mould has once formed, mere washing with water will not cleanse the bottle, but a drachm or two of strong Nitric Acid must be run round the sides to destroy the fungus, and prevent decomposition in the fresh solution. If Nitric Acid cannot be obtained, use Cyanide of Potassium; afterwards washing with abundance of water to remove the cleansing agent. With such precautions the developing solution will keep good for a week or longer.

It is a common practice with many in this process to make an addition of one grain of Pyrogallic Acid to each fluid ounce of the Gallic Acid solution; by which the rapidity of the development is materially increased.

The solution of Nitrate of Silver for use with the Gallic Acid may be made of the strength of twenty grains to the ounce. Some employ old Nitrate Bath for this purpose, but a separate solution of Nitrate of Silver is better, since it is free from Iodide of Silver, and cannot therefore deposit anything on dilution. About fifteen minims is a proper quantity to add to an ounce of Gallic Acid solution in cool weather: with less than this, defective development on the sky and other over-exposed parts would be encouraged.

Previous to the application of the developer, the surface of the film must be moistened with water, by holding it for an instant under a tap, and the plate should then be balanced on a levelling-stand. The glass ought to be laid quite flat, since if the Gallic Acid solution be allowed to drain down to one corner, the Negative will be unequally intense—a defect sometimes complained of, and only to be avoided by keeping the stratum of Gallo-Nitrate solution of equal depth.

A ready mode of levelling plates of middle size, is to cut a round hole in the top of a box, and to drop a funnel of glass or gutta-percha into it. Rest the glass upon the top of the funnel, and having poured the Gallic Acid solution over the film, move the funnel until the liquid covers the plate evenly.

The Writer invariably employs Dancer's developing dishes for Stereoscopic plates. They are moulded in one piece, and have a ledge of glass at each corner. About an ounce and a half of solution is required to fill the dish up to the ledge, and the plates are lowered on to the surface of the liquid by a bent pin, just as a sheet of salted paper is dropped upon a sensitizing solution. There is no difficulty in effecting this without the occurrence of air-bubbles, and as the film is not first wetted with water, the developer soon penetrates it, and acts with rapidity. Equal reduction throughout the entire surface of the image is secured, and if a deposit should form, it sinks to the bottom.

The only point to be observed with these glass dishes is to keep them chemically clean, for if a little reduced Silver be left in the corners, the Gallo-Nitrate will be discoloured thereby (p. 245). A bottle of waste Nitro-Sulphuric Acid which has been employed for making Pyroxyline, may be poured into the dish, the excess being returned again to the bottle, and the glass rinsed with abundance of water. Those who object to the use of strong acids may substitute the "Iodo-Cyanide of Potassium" described in the Appendix.

From half an hour to an hour must be allowed for the full development with Gallic Acid. It should be borne in mind, however, that the image in Taupenot's Process has a peculiar yellowish-green colour, and is far more opaque chemically than visually. Hence, if the mistake be made of developing up to the point which would be esteemed correct for a Collodion Negative, the plate will be nearly useless in printing. Beginners generally fail in this way, and are not aware that a Taupenot Negative which appears so translucent that the finger is distinctly seen by transmitted light behind the sky, will print a vigorous Positive.

In some cases where the reduction is retarded by cold, etc., it may be necessary to add a little more Nitrate of Silver towards the end of the development. Pour the Gallic Acid off the plate therefore into a clean measure, and if it be still colourless, drop into each ounce twenty minims of the twenty-grain solution as at first. If however turbidity or discoloration of developer is seen, the plate must be washed with water and the process recommenced with fresh solution.

The reason why Gallic Acid is recommended in preference to the more quicky acting Pyrogallic Acid, is because the latter is apt to discolour quickly, and to fog the surface of the film before the image is fully out. The Gallic Acid, although slower in action, is more certain, and penetrates the Albumen fully before it begins to reduce.

The employment of Pyrogallic Acid, however, in this process is not to be quite discarded. It is a law in Photography, that a strong developing agent will bring out an image after a shorter exposure than a weak developer; and therefore if, from too little time having been given in the Camera, the Gallo-Nitrate should fail in developing the dark parts of the object, the plate may be raised from the solution and the development completed with Pyrogallic Acid and Nitrate of Silver.

In ordinary cases also, when time is an object, the plate may be lifted off the Gallic Acid as soon as the image is fully out, and finished with Pyrogallic Acid; for the objection to the use of Pyrogallic Acid, above given, that it acts before the horny Albumen has been penetrated, scarcely applies when the film is previously softened by the action of the Gallic Acid. A second plate may be laid upon the same portion of Gallic Acid, and sometimes even a third, if the weather is cool and the chemicals and dishes are sufficiently pure to preserve the developer clear. This rapid mode of working however will succeed best in experienced hands, and beginners would be likely to make stains upon the film if they trusted too much to the employment of Pyrogallic Acid. With regard to such stains, it is one great advantage of Taupenot's process, that the film is usually sufficiently hard to allow of their being rubbed off with the finger or a small tuft of cotton wool.

Fixing solution.—Fix with a saturated solution of Hyposulphite in preference to Cyanide, and wash for double the time required in the case of a Collodion Negative (p. 308); after which the plate may be varnished in the usual way. Small blisters forming at this stage of the process will disappear on drying.

Failures.—The common failures are blistering—hardness of Negative, which makes it print black and white without half-tone—and markings upon the Negative.

The cause of blistering has already been partially explained at page 432, and the remedy on which experienced operators lay the most stress is perfect dryness of the film at every stage; it may be held to the fire before dipping in the Aceto-Nitrate Bath, and again previous to its exposure in the Camera. Those who attempt to economize waste Collodion and "bottoms" of bottles by using them in Taupenot's process must be prepared for wrinkling or blistering of the film, since an increase in the amount of Alcohol beyond a certain point appears to lessen the adhesion of the Collodion to the glass. Perfect security against blisters can only be obtained by coating the glasses with dilute Gelatine or Albumen before Collodionizing (p. 422).

Hardness of Negative is due to over-development, to the addition of too much Nitrate of Silver to the developer, or to under-exposure. The use of very powerful lenses should be mentioned as another cause. Taupenot's process is better fitted for long-focus lenses than for lenses of the Stereoscopic size.

Markings like those in the figure may be traced to the Collodion in the first instance, but the presence of Albumen exaggerates them. The Pyroxyline was made in too strong acids, and hence the structural arrangement. Much however may be done to remedy the markings by keeping the developing solution moving, and not allowing a stationary layer to rest upon the plate.

Marbled markings are often produced by an oily scum floating upon the Aceto-Nitrate Bath, and carried down by the film. A rapid discoloration and turbidity of the developer, causing a deposit on the shadows, may be due to chalk in the water used for the Gallic Acid, or to decomposition in the Aceto-Nitrate Bath by long contact with dissolved Albumen.

THE MODIFICATION OF MESSRS. PETSCHLER AND MANN.

It will not be advisable to attempt this modification with an unsuitable Collodion. The tendency to blistering is less than with Taupenot's process, but the image is more feeble, and hence greater attention must be paid to the state of the Collodion. Read the remarks at page 427, since it will be found that a Collodion in good order for Fothergill's process will answer likewise for the process now under discussion.

Clean the glasses, coat them with Collodion, and render them sensitive exactly as in Fothergill's process. Then wash *freely* under a tap, or with two or three changes of common water in a dish, after which the film will be ready for the Albumen.

To prepare the Albumen, take of

Albumen	1 fluid ounce.
Water	1 fluid ounce.
Chloride of Ammonium	3 grains.

Beat the whole to a perfect froth, and when it has again liquefied, filter it through paper, if possible; but when it refuses to run through the paper (which in the absence of Ammonia is not unlikely to happen) it must be passed two or three times through a double thickness of fine muslin, until all suspended particles are removed.

Apply this Albumen to the washed film, exactly as in Taupenot's process p. 435, and then dry the plates spontaneously, finishing with artificial heat, p. 430, after which they may be stowed away in a box.

The plates are at this stage nearly insensitive to light, and are well fitted for long keeping; but inasmuch as they do not appear to be quite insensitive, it will be better to prepare them by yellow light, and to keep them in a dark place until they are required for use.

In order to restore the sensitiveness, which the presence of free Chloride of Ammonium or Sodium in the film reduces to a minimum, wash the plates in two or three changes of common water, and then flood them gently with distilled water, after which they may be reared up to dry. A safe plan will be to leave each plate for a few minutes in the first washing water, so as to soften the Albumen, and thus to facilitate the removal of soluble matters.

From this point proceed in every respect as in Fothergill's process, but if the Negative should prove to be too metallic, and too deficient in contrast, it will be well in the next experiment to give the Albumen film a final wash of weak aqueous solution of Tannin. Dissolve two grains of Tannin in half an ounce of distilled water, and apply it twice to the film (half a grain of Gallic Acid would probably answer the same purpose). This proceeding will add much to the vigour of the Negative, but further trials are needed to confirm its practical value.

The inquiry has been made why stains during development are less frequently met with in this process than in the original one of M. Taupenot. The reason appears to be that in the latter the Nitrate of Silver is always slightly in excess, since the plates receive a final dip in the Aceto-Nitrate Bath: in the former however the Chloride of Sodium is the last application, and hence, although the rapidity of reduction is restrained, the developer remains for a longer time without becoming turbid. The same observation applies in a measure to the Fothergill process, in which also turbidity of developer is more rare than in some other dry processes.

END OF PART II.

PART III.

OUTLINES OF GENERAL CHEMISTRY.

OUTLINES OF GENERAL CHEMISTRY.

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CHAPTER I.

THE CHEMICAL ELEMENTS AND THEIR COMBINATIONS.

The limits of the present Work allow only of a sketch of the subjects which it is proposed to treat in this Chapter. Our attention therefore must be confined to an explanation of certain points which are alluded to in the First Part of the Work, and without a proper understanding of which it will be impossible for the reader to make progress.

The following division may be adopted:—The more important Elementary Bodies, with their symbols and atomic weights; the Compounds formed by their union; the class of Salts; illustrations of the nature of Chemical Affinity; Chemical Nomenclature; Symbolic Notation; the laws of Combination; the Atomic Theory; the Chemistry of Organic Bodies.

THE CHEMICAL ELEMENTS, WITH THEIR SYMBOLS AND ATOMIC WEIGHTS.

The class of elementary bodies embraces all those substances which cannot, in the present state of our knowledge, be resolved into simpler forms of matter.

The chemical elements are divided into "metallic" and "non-metallic," according to the possession of certain general characters.

The following are some of the principal non-metallic elements, with the symbols employed to designate them, and their atomic weights :*—

		Symbol.	Atomic Wt.
Gases.	Oxygen	O	8
	Hydrogen	H	1
	Nitrogen	N	14
	Chlorine	Cl	35·5
Solids.	Iodine	I	127
	Carbon	C	6
	Sulphur	S	16
	Phosphorus	P	31
Liquid.	Bromine	Br	80
Unknown.	Fluorine	F	19

The metallic elements are more numerous. The following list includes only those which are commonly known:—

		Symbol.	Atomic Wt.
Metals of the Alkalies.	Potassium	K	39
	Sodium	Na	23
	Lithium	L	7
Metals of the Alkaline Earths.	Barium	Ba	68·5
	Calcium	Ca	20
	Magnesium	Mg	12·16
Metals Proper.	Iron	Fe	28
	Zinc	Zn	32·7
	Cadmium	Cd	56
	Copper	Cu	31·7
	Lead	Pb	103·6
	Tin	Sn	59
	Arsenic	As	75
	Antimony	Sb	122
Noble Metals.	Mercury	Hg	100
	Silver	Ag	108
	Gold	Au	196·6
	Platinum	Pt	98·5

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* These atomic weights are taken from the second edition of Miller's 'Elements of Chemistry,' published by Parker and Son, West Strand.

ON THE BINARY COMPOUNDS OF THE ELEMENTS.

Many of the elementary bodies exhibit a tendency to combine with each other, and to form *compounds*. This attraction, termed "Chemical Affinity," is exerted principally between bodies which are opposed to each other in their general characters. Thus, taking for example the elements Chlorine and Iodine,—they are analogous in their reactions, and there is but little attraction between them; whereas either of the two will combine eagerly with Silver, which is an element of a different class. So, again, Sulphur unites with the metals, but two metallic elements are comparatively indifferent to each other.

Oxygen is by far the most important in the list of chemical elements. It combines with all the others, with the single exception, perhaps, of Fluorine. The attraction, or chemical affinity, however, which is exerted, varies much in different cases. The metals, as a class, are easily oxidized; whilst many of the non-metallic elements, such as Chlorine, Iodine, Bromine, etc., exhibit but little affinity for Oxygen. Nitrogen is also a peculiarly negative element, showing little or no tendency to unite with the others.

Classification of binary compounds containing Oxygen.—When one simple element unites with another, the product is termed a "binary" compound.

There are three distinct classes of binary compounds of Oxygen:—Neutral Oxides, basic Oxides, and acid Oxides.

Neutral and basic Oxides.—Take as examples, the Oxide of Hydrogen, or *Water*, a neutral Oxide; the Oxide of Potassium, or *Potash*, a basic Oxide.

Water is termed a *neutral* oxide, because its affinities are low, and it is comparatively indifferent to other bodies. Potash and Oxide of Silver are examples of *basic* oxides; but there is a great difference between the two in chemical energy, the former belonging to a superior class of bases, viz. the alkaline.

By studying the properties of an alkali (such as Potash or Soda) which are familiar to all, we gain a correct notion

of the whole class of basic oxides. An alkali is a subst
readily soluble in water, and yielding a solution which
a slimy feel from its solvent action upon the skin. It
mediately restores the blue colour of reddened litmus,
changes the blue infusion of cabbage to green. Last
is neutralized and loses all its characteristic properties
the addition of an acid.

The *weaker bases* are, as a rule, sparingly or not
soluble in water, neither have they the same caustic
solvent action upon the skin ; but they restore the c
of reddened litmus, and neutralize acids in the same
ner as the more powerful bases, or alkalies.

The Acid *Oxides*.—This class, taking the stronger
as the type, may be described as follows :—Very solu
water, the solution possessing an intensely sour taste,
a *corroding* rather than a solvent action upon the skin
acid changes the blue colour of litmus and other veg
substances to red, and neutralizes the alkalies and
oxides generally.

Observe however that these properties are possess
very various degrees by different acids. Prussic Acid
Carbonic Acid, for instance, are not sour to the taste,
being feeble in their reactions, redden litmus scarce
not at all. All acids however, without any exception,
to combine with bases and to neutralize themselves
that this may be said to be the characteristic proper
the class.

Chemical composition of Acid and Basic Oxides
trasted.—It is a law commonly observed, although
some exceptions, that bases are formed by the uni
Oxygen with *metals ;* and acids, by Oxygen uniting
non-metallic elements. Thus, Sulphuric Acid is a
pound of Sulphur and Oxygen: Nitric Acid, of Nitr
and Oxygen. But the alkali Potash is an oxide o
metal Potassium; and the oxides of Iron, Silver,
etc., are bases, and not acids.

Again, the composition of acids and bases is diff
in another respect; the former invariably contain

Oxygen in proportion to the other element than the latter. Taking the same examples as before, the two classes may be represented thus:—

Acids	Oil of Vitriol,	Sulphur	1 atom,	Oxygen 3 atoms.
	Aqua-fortis,	Nitrogen	1 „	Oxygen 5 „
Bases	Oxide of Silver,	Silver	1 atom,	Oxygen 1 atom.
	Oxide of Iron,	Iron	1 „	Oxygen 1 „

The class of Hydrogen Acids.—Oxygen is so essentially the element which forms the acidifying principle of acids, that its very name is derived from that fact (οξυς, acid, and γενναω, to generate). Still there are exceptions to this rule, and in some acids *Hydrogen* appears to play the same part; the *Hydracids*, as they are termed, are formed principally by Hydrogen uniting with elements like Chlorine, Bromine, Iodine, Fluorine, etc. Thus, Muriatic or Hydrochloric Acid contains Chlorine and Hydrogen; Hydriodic Acid contains Iodine and Hydrogen.

Observe, however, that the position held by the Hydrogen in these compounds, is different from that of the Oxygen in the "Oxyacids," as regards the number of atoms usually present; thus—

Aqua-fortis	= Nitrogen	1 atom,	Oxygen 5 atoms,
Muriatic Acid	= Chlorine	1 „	Hydrogen 1 atom;

so that the composition of the Hydracids is analogous to the *basic* oxides, in containing a single atom of each constituent.

THE TERNARY COMPOUNDS OF THE ELEMENTS.

As the various elementary substances unite with each other to form Binary Compounds, so these binary compounds again unite and form *Ternary* Compounds.

Compound bodies however do not, as a rule, unite with simple elements. In illustration, take the action of Nitric Acid upon Silver, described at page 12. No effect is produced upon the metal until *Oxygen* is imparted; then the Oxide of Silver so formed dissolves in the Nitric Acid. In other words, it is necessary that a binary compound should be first formed, before the solution can take place. The mutual attraction or chemical affinity exhibited by compound bodies is, as in the case of elements, most strongly marked when the two substances are opposed to each other in their general properties.

Thus, *acids* do not unite with other acids, but they combine instantly with *alkalies or basic oxides*, the two mutually neutralizing each other and forming "a salt."

Salts therefore are compounds produced by the union of acids and bases; common Salt, formed by neutralizing Hydrochloric Acid with Soda, being taken as the type of the whole class.

General characters of the Salts.—An aqueous solution of Chloride of Sodium, or common Salt, possesses those characters which are usually termed saline; it is neither sour nor corrosive, but, on the other hand, has a cooling agreeable taste. It produces no effect upon litmus and other vegetable colours, and is wanting in those energetic reactions which are characteristic of both acids and alkalies. Although formed by the union of two binary compounds, it differs essentially in properties from both.

All salts however do not correspond to this description of the properties of Chloride of Sodium. The Carbonate of Potash, for instance, is an acrid and alkaline salt, and the Nitrate of Iron reddens litmus-paper. A perfectly neutral salt is formed, when a strong acid unites with an energetic base; but if, of the two constituents, one is more powerful than the other, the properties of that one are often seen in the resulting salt. Thus the Carbonate of Potash is *alkaline* to test-paper, because the Carbonic Acid is feeble in its reactions; but if *Nitric Acid* and *Potash* are brought together, then a Nitrate of Potash is produced, which is neutral in every sense of the term.

The Chloride of Sodium and salts of a similar kind are freely soluble in water, but all salts are not so. Some dissolve only sparingly, and others not at all. The Chloride and Iodide of Silver are examples of the latter class; they are not bitter and caustic like the Nitrate of Silver, but are perfectly tasteless from being insoluble in the fluids of the mouth.

It is seen therefore from these examples, and many others which might be adduced, that the popular notion of a saline body is far from being correct, and that, in the language of strict definition, any substance is a salt which is produced by the union of an acid with a base, independent of the properties it may possess.

Thus the poisonous substance Cyanide of Potassium is a true salt; Nitrate of Silver is a salt; the green Sulphate of Iron is a Salt; so also is Chalk or Carbonate of Lime, which has neither taste, colour, nor smell.

On the "Hydracid" class of Salts.—The distinction between Oxyacids and Hydracids has already been pointed out (p. 451), the latter having been shown to consist of Hydrogen united with elements analogous in their reactions to Chlorine, Iodine, Bromine, etc.

In a salt formed by an Oxygen Acid, both the basic and acid elements appear. Thus the common *Nitre*, which is a Nitrate of Potash, is found by analysis to contain Oxide of Potassium as a base, in a state of combination with Nitric Acid. But if a salt be formed by neutralizing an alkali with *a Hydrogen Acid*, the product in that case does not contain all the elements. This is seen from the following example:—

Hydrochloric Acid + Soda
= Chloride of Sodium + Water;

or, stated more at length,—

(Chlorine Hydrogen) + (Oxygen Sodium)
= (Chlorine Sodium) + (Oxygen Hydrogen)

Observe that the Hydrogen and Oxygen being present in the correct proportions, unite to form Water, which is an Oxide of Hydrogen. This water passes off when the solution is evaporated, and leaves the dry crystals of salt. On the other hand, with the Oxyacid Salts, the elementary Hydrogen being absent, no water is formed, and the Oxygen remains.

It must therefore be borne in mind that salts like the Chlorides, Bromides, Iodides, etc., contain only *two* elements; but that in the Oxyacid Salts, such as Sulphates, Nitrates, Acetates, *three* are present. Thus, Nitrate of Silver consists of Nitrogen, Oxygen, and Silver, but Chloride of Silver contains simply Chlorine and metallic Silver united, without Oxygen.

The Hydracid salts however, when decomposed, yield products similar to the Oxyacid salts. For instance if Iodide of Potassium be dissolved in water, and dilute Sulphuric Acid added, this acid being powerful in its chemical affinities, tends to appropriate to itself the alkali; it does not however remove *Potassium* and liberate *Iodine*, but takes the *Oxide* of Potassium and sets free *Hydriodic Acid*. In other words, as an atom of water is produced during the *formation* of a Hydracid Salt, so is an atom destroyed and made to yield up its elements, in the *decomposition* of a Hydracid Salt.

The reaction of dilute Sulphuric Acid upon Iodide of Potassium may be stated thus:—

Sulphuric Acid *plus* (Iodine Potassium) *plus* (Hydrogen Oxygen)
equals (Sulphuric Acid, Oxygen Potassium) or Sulphate of Potash,
and (Hydrogen Iodine) or Hydriodic Acid.

THE NATURE OF CHEMICAL AFFINITY FURTHER ILLUSTRATED.

Illustration from the Non-metallic Elements.—If a stream of Chlorine gas be passed into a solution containing the same salt as before mentioned, viz. the Iodide of Potassium, the result is to liberate a certain portion of Iodine, which dissolves in the liquid, and tinges it of a brown colour. The element Chlorine, possessing a degree of chemical energy superior to that of Iodine, prevails over it, and removes the Potassium with which the Iodine was previously combined.

$$\text{Chlorine} + \text{Iodide of Potassium}$$
$$= \text{Iodine} + \text{Chloride of Potassium.}$$

The same Law illustrated by the Metals.—A strip of Iron dipped in solution of Nitrate of Silver becomes immediately coated with Metallic Silver; but a piece of Silver-foil may be left for any length of time in Sulphate of Iron without undergoing change: the difference depends upon the fact, that metallic Iron has a greater attraction for Oxygen than Silver has, and hence it displaces it from its solution.

Iron + Nitrate of Silver
= Silver + Nitrate of Iron.

Illustrations amongst Binary Compounds.—If a few drops of solution of Potash be added to solution of Nitrate of Silver, a brown deposit is formed, which is the Oxide of Silver, sparingly soluble in water. That is to say, as a stronger *metal* displaces *metallic Silver*, so does an *oxide* of the same metal displace *Oxide of Silver*. Therefore bases like the alkalies, alkaline earths, etc., cannot exist in a free state in solutions of the salts of weaker bases,—a liquid containing Nitrate of Silver could not also contain free Potash or Ammonia.

In the list given at page 448, the metallic elements are arranged principally in the order of their chemical affinities; those of Potassium, Sodium, Barium, etc., being the most marked.

As the alkalies displace the weaker bases from their combination with acids, so the strong *acids* displace weak acids from their combination with bases. Thus, as

Oxide of Potassium + Acetate of Silver
= Oxide of Silver + Acetate of Potash;

So

Nitric Acid + Acetate of Silver
= Acetic Acid + Nitrate of Silver.

In the list of acids, Sulphuric Acid is usually placed first as being the strongest, and Carbonic Acid, a gaseous substance, last. The vegetable acids, such as Acetic, Tartaric, etc., are *intermediate*, being weaker than the mineral acids, but stronger than Carbonic, or Hydrocyanic Acid.

The order of decompositions affected by the insolubility *or the volatility of the products which may be formed.*—It might be inferred from remarks already made, that on mixing saline solutions, a gradual interchange of elements would take place, until the strongest acids were associated with the strongest bases, and *vice versâ.* There are many causes however which interfere to prevent this; one of which is *volatility.*—

The violent effervescence which takes place on treating a *Carbonate* of any kind with an acid is due to the *gaseous* nature of Carbonic Acid and its escape in that form, which greatly facilitates the decomposition.

Insolubility is also a cause which exercises a great influence on the result which will follow in mixing solutions. If the formation of an insoluble substance be possible by any interchange of elements, it will take place. A solution of Chloride of Sodium added to Nitrate of Silver invariably produces Chloride of Silver; the *insolubility* of Chloride of Silver being the cause which determines its formation.

So again, Sulphate of Lead and Protonitrate of Iron are produced by mixing Nitrate of Lead with Sulphate of Iron; but if Nitrate of *Potash* be substituted for Nitrate of Lead, the result is uncertain, because there are no elements present which can, by interchanging, form an insoluble salt; Sulphate of Potash, although *sparingly* soluble in water, is not *insoluble*, like the Sulphate of Lead or the Sulphate of Baryta.

ON CHEMICAL NOMENCLATURE.

The nomenclature of the chemical *elements* is mostly independent of any rule; but an attempt has been made to obviate this in the case of those of later discovery. Thus the names of the newly-found *metals* usually end in *um*, as Potassium, Sodium, Barium, Calcium, etc.; and those elements which possess analogous characters have corresponding terminations assigned to them, as Chlorine, Bromine, Iodine, Fluorine, etc.

Nomenclature of Binary Compounds.—These are often named by attaching the termination *ide* to the more important element of the two: as the Ox*ide* of Hydrogen, or Water; the Chlor*ide* of Silver; the Sulph*ide* of Silver.

When the same body combines with Oxygen, or the corresponding element, in more than one proportion, the prefix *proto* is applied to that containing the least Oxygen; *sesqui* to that with once and a half as much as the *proto; bi* or *bin* to that with twice as much; and *per* to the one containing the most Oxygen of all. As examples, take the following:—The Protoxide of Iron; the Sesquioxide of Iron; the Protochloride of Mercury; the Bichloride of Mercury. In these examples the Sesquioxide of Iron is also a *Per*oxide, because no higher simple oxide is known, and the Bichloride of Mercury is a *Per*chloride for a similar reason.

When an inferior compound is discovered, it is often termed *sub;* as the Suboxide of Silver, the Subchloride of Silver. These bodies contain the least known quantity of Oxygen and Chlorine respectively, and are hence entitled to the prefix *proto;* but being of minor importance, they are excepted from the general rule.

The combinations of metallic elements with each other are termed "alloys:" or if containing Mercury, "amalgams."

Nomenclature of Binary Compounds possessing acid properties.—These are named on a different principle. The termination *ic* is applied to one element. Thus, taking as an illustration the liquid known as "Oil of Vitriol," it is truly an *Oxide* of Sulphur, but as it possesses strong acid properties it is termed Sulphuric *Acid.* So Nitric Acid is an Oxide of Nitrogen; Carbonic Acid is an Oxide of Carbon, etc. When there are two oxides of the same element, both possessing acid properties, the most important has the termination *ic,* and the other *ous;* as Sulphuric Acid, Sulphur*ous* Acid; Nitric Acid, Nitr*ous* Acid.

Nomenclature of the Hydracids.—The Hydrogen Acids are distinguished from Oxyacids by retaining the names of both constituents, the termination *ic* being annexed as usual. Thus, *Hydro*chloric Acid, or the Chloride of Hydrogen; *Hydr*iodic Acid, or the Iodide of Hydrogen.

Further illustrations of the nomenclature of Binary Compounds.—The Oxides of Nitrogen, and also of Sulphur, afford an interesting illustration of the principles of nomenclature. The former are as follows:—

	Nitrogen.	Oxygen.
Protoxide of Nitrogen . . .	1 atom.	1 atom.
Binoxide of Nitrogen . . .	1 „	2 „
Nitrous Acid	1 „	3 „
Peroxide of Nitrogen . . .	1 „	4 „
Nitric Acid	1 „	5 „

Observe, that two only out of the five possess acid properties, the others being simple oxides. Nitric Acid is, strictly speaking, the "Peroxide," but as it belongs to the class of acids, that term naturally falls to the compound below.

The binary compounds of Sulphur with Oxygen all possess acid properties; they may be represented (in part) as follows:—

	Sulphur.	Oxygen.
Hyposulphurous Acid . . .	2 atoms.	2 atoms.
Sulphurous Acid	1 „	2 „
Hyposulphuric Acid . . .	2 „	5 „
Sulphuric Acid	1 „	3 „

In this case the Sulphuric and Sulphurous Acids had become familiarly known before the others, intermediate in composition, were discovered. Hence, to avoid the confusion which would result from changing the nomenclature, the new bodies are termed *Hypo*sulphuric and *Hypo*sulphurous (from ὑπο, *under*).

Nomenclature of Salts.—Salts are named according to the acid they contain; the termination *ic* being changed into *ate*, and *ous* into *ite*. Thus, Sulphuric Acid forms Sulph*ates;* Nitric Acid, Nitr*ates;* but Sulphur*ous* Acid forms Sulph*ites*, and Nitrous Acid, Nitr*ites*.

In naming a salt, the base is always placed *after* the acid, the term *oxide* being omitted: thus, *Nitrate of Oxide of Silver* is more shortly known as "Nitrate of Silver," the presence of Oxygen being understood.

When there are two oxides of the same base, both of which are *salifiable,*—in naming the salts, the term *proto* is prefixed to the acid of the salt formed by the lower, and *per* to that of the higher oxide; as the *Proto*sulphate of Iron, or Sulphate of the Protoxide: the *Per*sulphate of Iron, or Sulphate of the Peroxide.

Many salts contain more than one atom of acid to each atom of base. In that case, the usual prefixes expressive of quantity are adopted: thus, the *Bi*sulphate of Potash contains twice as much Sulphuric Acid as the neutral Sulphate, etc.

On the other hand, there are salts in which the base is in excess with regard to the acid, and which are usually known as "basic salts;" thus, the red powder which deposits from solution of Sulphate of Iron, is a *basic* Persulphate of Iron, or a Sulphate of the Peroxide of Iron with more than the normal proportion of oxide.

Nomenclature of the Hydracid Salts.—The composition of these salts being different from those formed by Oxygen Acids, the nomenclature varies also. Thus, in neutralizing Hydrochloric Acid with Soda, the product formed is not known as Hydrochlorate of Soda, but as *Chloride of Sodium;* this salt, and others of a similar constitution, being *binary,* and not *ternary,* compounds. The salt produced by Hydrochloric Acid and *Ammonia* however is often called "Muriate or Hydrochlorate of Ammonia," although more strictly it should be the *Chloride of Ammonium.*

ON SYMBOLIC NOTATION.

The list of symbols employed to represent the various elementary bodies is given at page 448.—Commonly the nitial letter of the Latin name is used, a second or smaller etter being added when two elements correspond in their nitials: thus C stands for Carbon, Cl for Chlorine, Cd for Cadmium, and Cu for Copper.

The chemical symbol however does not simply represent a particular element; it denotes also a definite weight, or equivalent proportion of that element. This will be explained more fully in the succeeding pages, when we speak of the Laws of Combination.

Formulæ of Compounds.—In the *nomenclature* of compounds it is usual to place the Oxygen or analogous element *first* in the case of binary compounds, and the acid before the base in the ternary compounds, or salts; but in representing them *symbolically* this order is reversed: thus, Oxide of Silver is written AgO, and never as OAg; Nitrate of Silver as $AgO\ NO_5$, not NO_5AgO.

The juxtaposition of symbols expresses combination; thus, FeO is a compound of one proportion of Iron with one of Oxygen, or the "Protoxide of Iron." If more than one equivalent be present, small figures are placed below the symbols: thus, Fe_2O_3 represents two equivalents of Iron united with three of Oxygen, or the "Peroxide of Iron;" SO_3, one equivalent of Sulphur with three of Oxygen, or Sulphuric Acid.

Larger figures placed before and in the same line with the symbols, affect the *whole compound* which the symbols express: thus, $2\ SO_3$ means two equivalents of Sulphuric Acid; $3\ NO_5$, three equivalents of Nitric Acid. The interposition of a comma prevents the influence of the large figure from extending further. Thus, the double Hyposulphite of Soda and Silver is represented as follows:—

$$2\ NaO\ S_2O_2,\ AgO\ S_2O_2,$$

or *two* equivalents of Hyposulphite of Soda with *one* of Hyposulphite of Silver; the large figure referring only to the first half of the formula. Sometimes brackets, etc., are employed, in order to render a complicated formula more plain. For example, the formula for the double Hyposulphite of Gold and Soda, or "Sel d'or," may be written thus:—

$$3(NaO\ S_2O_2)\ AuO\ S_2O_2+4\ HO.$$

In this formula, the *plus* sign (+) denotes that the four atoms of water which follow, are less intimately united with the framework of the salt than the other constituents.

The use of a *plus* sign is commonly adopted in representing salts which contain water of crystallization. Thus, the formula for the crystallized Protosulphate of Iron is written as follows:—

$$FeO\ SO_3 + 7\ HO.$$

These atoms of water are driven off by the application o heat, leaving a white substance, which is the anhydrous salt, and would be written simply as $FeO\ SO_3$.

The *plus* sign however is often employed in token of simple *addition*, no combination of any kind being intended. Thus the decomposition which follows on mixing Chloride of Sodium with Nitrate of Silver may be written as follows:—

$$NaCl + AgO\ NO_5 = AgCl + NaO\ NO_5;$$

that is,—

Chloride of Sodium *added to* Nitrate of Silver
equals Chloride of Silver *and* Nitrate of Soda.

ON EQUIVALENT PROPORTIONS.

When elementary or compound bodies enter into chemical union with each other, they do not combine in indefinite proportions, as in the case of a mixture of two liquids, or the solution of a saline body in water. On the other hand, a definite weight of the one unites with an equally definite weight of the other; and if an excess of either be present, it remains free and uncombined.

Thus, if we take a *single grain* of the element Hydrogen —to convert that grain into Water there will be required exactly 8 grains of Oxygen; and if a larger quantity than his were added, as for instance *ten grains*, then two grains would be over and above. So, to form *Hydrochloric Acid*, grain of Hydrogen takes 35·5 grains of Chlorine:—for he *Hydriodic Acid*, 1 grain of Hydrogen unites with 127 rains of Iodine.

Again, if separate portions of metallic Silver, of 108 grains each, are weighed out,—in order to convert them into Oxide, Chloride, and Iodide of Silver respectively, there would be required

Oxygen	8 grains.
Chlorine	35·5 „
Iodine	127 „

Therefore it appears that 8 grains of Oxygen are *equivalent* to 35·5 grains of Chlorine and to 127 grains of Iodine, seeing that these quantities all play the same part in combining; and so it is with regard to the other elements,—to every one of them a figure can be assigned which represents the number of parts by weight in which that element unites with others. These figures are the "equivalents" or "combining proportions," and they are denoted by the *symbol* of the element. A symbol does not stand as a simple representative of an element, but as a representative of *one equivalent* of an element. Thus "O" indicates 8 parts by weight of Oxygen; "Cl" one equivalent, or 35·5 parts by weight, of Chlorine; and so with the rest.

Observe however that these figures, termed "equivalents," do not refer to the *actual number of parts* by weight, but only to the *ratio* which exists between them: if Oxygen be 8, then Chlorine will be 35·5: but if we term Oxygen 100, as some have proposed, then Chlorine would be 443·75.

In the scale of equivalents now usually adopted, Hydrogen, as being the lowest of all, is taken as unity, and the others are related to it.

Equivalents of Compounds.—The law of equivalent proportions applies to compounds as well as to simple bodies, the combining proportion of a compound being always the *sum* of the equivalents of its constituents. Thus Sulphur is 16, and Oxygen 8, therefore Sulphuric Acid, or SO_3, equals 40. The equivalent of Nitrogen being 14, that of Nitric Acid, or NO_5, is 54.

The same rule applies with regard to salts. Take for instance the Nitrate of Silver: it contains

	Equivalent.
Nitrogen	14
6 Oxygen.	48
Silver	108
Total of equivalents, or equivalent of the Nitrate of Silver } .	170

Practical application of the Laws of Combination.—The utility of being acquainted with the law of combining proportions is obvious when their nature is understood. As bodies both unite with and replace each other in equivalents, a simple calculation shows at once how much of each element or compound will be required in a given reaction. Thus, supposing it be desired to convert 100 grains of Nitrate of Silver into *Chloride* of Silver, the weight of Chloride of Sodium which will be necessary is deduced thus:—one equivalent, or 170 parts, of Nitrate of Silver is decomposed by an equivalent, or 58·5 parts, of Chloride of Sodium. Therefore

as 170 : 58·5 : : 100 : 34·4;

that is, 34·4 grains of Salt will precipitate, in the state of Chloride, the whole of the Silver contained in 100 grains of Nitrate.

So again, in order to form the Iodide of Silver, the proportions in which the two salts should be mixed is thus shown. The equivalent of Iodide of Potassium is 166, and that of Nitrate of Silver is 170. These numbers so nearly correspond, that it is common to direct that *equal weights* of the two salts should be taken.

One more illustration will suffice. Supposing it be required to form 20 grains of Iodide of Silver—how much Iodide of Potassium and Nitrate of Silver must be used? One equivalent, or 166 parts, of Iodide of Potassium, will yield an equivalent, or 235 parts, of Iodide of Silver; therefore

as 235 : 166 : : 20 : 14·12.

Hence, if 14·12 grains of the Iodide of Potassium be dissolved in water, and an equivalent quantity, viz. 14·46 grains, of the Nitrate of Silver added, the yellow precipitate, when washed and dried, will weigh precisely 20 grains.

ON THE ATOMIC THEORY.

The atomic theory, originally proposed by Dalton, so much facilitates the comprehension of chemical reactions generally, that it may be useful to give a short sketch of it.

It is supposed that all matter is made up of an infinite number of minute atoms, which are elementary, and do not admit of further division. Each of these atoms possesses an actual weight, although inappreciable by our present methods of investigation. Simple atoms, by uniting with each other, form *compound atoms:* and when these compounds are broken up, the elementary constituent atoms are not destroyed, but separate from each other, in possession of all their original properties.

In representing the simple atomic structure of bodies, *circles* may be used, as in the following diagram.

Fig. 1 is a compound atom of Sulphuric Acid, consisting of an atom of Sulphur united intimately with three of Oxygen; fig. 2 is an atom of Peroxide of Nitrogen, NO_4; and fig. 3, an atom of Nitric Acid, composed of Nitrogen 1 atom, Oxygen 5 atoms, or in symbols NO_5.

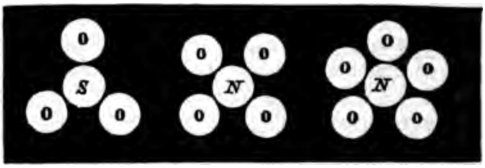

Fig. 1. Fig. 2. Fig. 3.

The term "atomic weight" substituted for equivalent proportion.—If we suppose that the simple atoms of different kinds of matter *differ in weight,* and that this difference is expressed by their equivalent numbers, the whole laws of combination follow by the simplest reasoning. It is easy to understand that an atom of one element, or compound, would displace, or be substituted for, a single atom of another; therefore, taking as the illustration the decomposition of Iodide of Potassium by Chlorine,—the weight of the latter element required to liberate 127 grains of Iodine is 35·5 grains, *because the weights of the atoms of those two elementary bodies are as* 35·5 *to* 127. So again, in the reaction between Chloride of Sodium and Nitrate of Silver, a compound atom of the former, represented by the weight 58·5, reacts upon a compound atom of the latter, which equals 170.

Therefore in place of the term "equivalent" or "combining proportion," it is more usual to employ that of "atomic weight." Thus the atomic weight of Oxygen is 8, represented by the symbol O; that of Sulphur is 16; hence the atomic weight of the compound atom of Sulphuric Acid, or SO_3, is necessarily equal to the combined weights of the four simple atoms; *id est,* $16 + 24 = 40$.

ON THE CHEMISTRY OF ORGANIC SUBSTANCES.

By "organic" substances are meant those which have ossessed *life,* with definite organs and tissues, in contralistinction to the various forms of dead inorganic matter, in which no structural organization of that kind is found.

The term organic however is also applied to substances which are obtained by chemical processes from the vegetale and animal kingdoms, although they cannot themselves e said to be living bodies; thus Acetic Acid, procured by he distillation of woody fibre, and Alcohol, by fermentaon from sugar, are considered as organic substances.

The class of organic bodies embraces a great variety of roducts; which, like inorganic Oxides, may be divided to neutral, acid, and basic.

The organic *acids* are numerous, including Acetic Acid artaric, Citric, and a variety of others.

The *neutral substances* cannot easily be assimilated to y class of inorganic compounds; as examples, take arch, Sugar, Lignine, etc.

The *bases* are also a large class. They are mostly rare substances, not familiarly known: Morphia, obtained from Opium; Quinia, from Quinine; Nicotine, from Tobacco, are illustrations.

Composition of organic and inorganic bodies contrasted. —There are more than fifty elementary substances found in the inorganic kingdom, but only *four*, commonly speaking, in the organic: these four are Carbon, Hydrogen, Nitrogen, and Oxygen.

Some organic bodies,—oil of turpentine, naphtha, etc., contain only Carbon and Hydrogen; many others, such as sugar, gum, alcohol, fats, vegetable acids—Carbon, Hydrogen, and Oxygen. The *Nitrogenous bodies*, so called, containing Nitrogen in addition to the other elements, are principally substances derived from animal and vegetable tissues, such as Albumen, Caseine, Gelatine, etc.; Sulphur and Phosphorus are also present in many of the Nitrogenous bodies, but only to a small extent.

Organic substances, although simple as regards the *number* of elements involved in their formation, are often highly complex in the arrangement of the atoms; this may be illustrated by the following formulæ:—

Starch	$C_{24}H_{20}O_{20}$
Lignine	$C_{24}H_{20}O_{20}$
Cane Sugar	$C_{24}H_{22}O_{22}$
Grape Sugar	$C_{24}H_{28}O_{28}$

Inorganic bodies, as already shown, unite *in pairs*,—two elements join to form a binary compound; two binary compounds produce a salt; two salts associated together form a double salt. With organic bodies however the arrangement is different,—the elementary atoms are all grouped equally in one compound atom, which is highly complex in structure, and cannot be split up into binary products.

Observe also, as characteristic of Organic Chemistry, the apparent similarity in composition between bodies which differ widely in properties. As examples take *Lig-*

nine, or cotton fibre, and *Starch*,—each of which contains the three elements united as $C_{24}H_{20}O_{20}$.

Mode of distinguishing between Organic and Inorganic matter.—A simple means of doing this is as follows:—place the suspected substance upon a piece of Platinum-foil, and heat it to redness with a spirit-lamp: if it first *blackens*, and then burns completely away, it is probably of organic origin. This test depends upon the fact, that the constituent elements of organic bodies are all either themselves volatile, or capable of forming volatile combinations with Oxygen. Inorganic substances, on the other hand, are often unaffected by heat, or, if volatile, are dissipated without previous charring.

The action of heat upon organic matter may further be illustrated by the combustion of coal or wood in an ordinary furnace;—first, an escape of Carbon and Hydrogen, united in the form of volatile gaseous matter, takes place, leaving behind a black cinder, which consists of Carbon and inorganic matter combined; afterwards this Carbon burns away into Carbonic Acid, and a grey ash is left which is composed of inorganic salts, and is indestructible by heat.

CHAPTER II.

VOCABULARY OF PHOTOGRAPHIC CHEMICALS.*

ACETIC ACID.

Symbol, $C_4H_3O_3+HO$. Atomic weight, 60.

ACETIC Acid is a product of the *oxidation* of Alcohol. Spirituous liquids, when perfectly pure, are not affected by exposure to air; but if a portion of yeast, or Nitrogenous organic matter of any kind, be added, it soon acts as a *ferment*, and causes the spirit to unite with oxygen derived from the atmosphere, and so to become *sour* from formation of Acetic Acid, or "vinegar."

Acetic Acid is also produced on a large scale by heating *wood* in close vessels: a substance distils over which is Acetic Acid contaminated with empyreumatic and tarry matter; it is termed Pyroligneous Acid, and is much used in commerce.

The most concentrated Acetic Acid may be obtained by neutralizing common vinegar with Carbonate of Soda, and crystallizing out the Acetate of Soda so formed; this Acetate of Soda is then distilled with Sulphuric Acid, which removes the Soda and liberates Acetic Acid: the Acetic Acid being volatile, distils over, and may be condensed.

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* N.B. The arrangement in this Vocabulary is made with reference to the principal constituent, in the case of compounds. Thus, *Acetic Ether* will be found under the head of "Ether, Acetic," *Nitrate of Silver* as "Silver, Nitrate of," *Iodide of Potassium* as "Potassium, Iodide of," etc.

Properties of Acetic Acid.—The strongest acid contains only a single atom of water; it is sold under the name of "Glacial Acetic Acid," so called from its property of solidifying at a moderately low temperature. At about 50° the crystals melt, and form a limpid liquid of pungent odour and a density nearly corresponding to that of water; the specific gravity of Acetic Acid however is no test of its real strength, which can only be estimated by analysis.

The commercial *Glacial* Acetic Acid so termed is usually diluted with water, and sometimes a trace of Sulphurous Acid is introduced, as the Writer is informed, to confer the property of solidifying in cold weather, and thus to give an appearance of strength. Sulphurous and Hydrochloric Acids are both injurious in Photographic Processes, from their property of precipitating Nitrate of Silver. To detect them proceed as follows:—dissolve a small crystal of Nitrate of Silver in a few drops of water, and add to it about half a drachm of the Glacial Acid; the mixture should remain quite clear even when exposed to light. Hydrochloric, and Sulphurous Acid produce a white deposit of Chloride or Sulphite of Silver; and if *Aldehyde* or volatile tarry matter be present in the Acetic Acid, the mixture with Nitrate of Silver, although clear at first, becomes discoloured by the action of light.

Glacial Acetic Acid sometimes has a smell of garlic. In this case it probably contains an organic Sulphur Acid, and is unfit for use.

Many employ a cheaper form of Acetic Acid, sold by druggists as "Beaufoy's" acid; it should be of the strength of the Acetic Acid fortiss. of the London Pharmacopœia, ontaining 30 per cent. real Acid. It will be advisable o test it for Sulphuric Acid (see Sulphuric Acid), and ther impurities, before use. When a certain quantity f the Glacial Acid is advised in a formula, take three imes as much of the Beaufoy's Acid. The Writer freuently uses it, and finds it more constant in its properties han the "Glacial Acid" so called.

ALBUMEN.

Albumen is an organic principle found both in the animal and vegetable kingdom. Its properties are best studied in the *white of egg*, which is a very pure form of Albumen.

Albumen is capable of existing in two states; in one of which it is soluble, in the other insoluble in water. The aqueous solution of the soluble variety gives a slightly alkaline reaction to test-paper; it is somewhat thick and glutinous, but becomes more fluid on the addition of a small quantity of an alkali, such as Potash or Ammonia.

Soluble Albumen may be converted into the *insoluble* form in the following ways:—

1. *By the application of heat.*—A moderately strong solution of Albumen becomes opalescent and coagulates on being heated to about 150° Fahrenheit, but a temperature of 212° is required if the liquid is very dilute. A layer of *dried* Albumen cannot easily be coagulated by the mere application of heat.

2. *By addition of strong acids.*—Nitric Acid coagulates Albumen perfectly without the aid of heat. Acetic Acid however acts differently, appearing to enter into combination with the Albumen, and forming a compound soluble in warm water acidified by Acetic Acid.

3. *By the action of metallic salts.*—Many of the salts of the metals coagulate Albumen completely. Nitrate of Silver does so; also the Bichloride of Mercury. Ammoniacal Oxide of Silver however does not coagulate Albumen.

The white precipitate formed on mixing Albumen with Nitrate of Silver is a chemical compound of the animal matter with Protoxide of Silver, and has been termed Albuminate of Silver: its properties have been described at pp. 20 and 231. On heating in a current of Hydrogen gas, it assumes a brick-red colour, being probably reduced to the condition of an organic compound of a *Suboxide* of Silver. It is then almost insoluble in Ammonia, but enough dissolves to tinge the liquid wine-red. The *red coloration* of solution of Nitrate of Silver employed in sensitizing the Albuminized Photographic paper is doubtless produced by the same compound, although often referred to the presence of Sulphide of Silver.

Albumen also combines with Lime and Baryta. When Chloride of Barium is used with Albumen, a white precipitate of this kind usually forms.

By long keeping, Albumen loses its alkaline reaction and becomes sour and more limpid than at first. Mucous threads like cobwebs form in it, which appear to be caused by oxidation. Ammonia added to Albumen is said to preserve it for a longer time, and a lump of camphor floated in the liquid has also a good effect. Decomposed Albumen usually contains Sulphuretted Hydrogen.

Chemical composition of Albumen.—Albumen belongs to the *Nitrogenous* class of organic substances (see page 466). It also contains small quantities of Sulphur and Phosphorus; when burnt, it leaves behind an ash in which Chloride and Phosphate can be detected.

ALCOHOL.

Symbol, $C_4H_6O_2$. Atomic weight, 46.

Alcohol is obtained by the careful distillation of any spirituous or fermented liquor. If wine or beer be placed in a retort, and heat applied, the Alcohol, being more volatile than water, rises first, and may be condensed in an appropriate receiver; a portion of the vapour of water however passes over with the Alcohol, and dilutes it to a certain extent, forming what is termed "Spirits of Wine." Much of this water may be removed by redistillation from Carbonate of Potash; but in order to render the Alcohol thoroughly *anhydrous*, it is necessary to employ *quicklime*, which possesses a still greater attraction for water. An equal weight of this powdered lime should be mixed with strong Alcohol of ·823, and the two be distilled together.

Properties of Alcohol.—Pure anhydrous or absolute Alcohol is a limpid liquid, of an agreeable odour and pungent taste; sp. gr. at 60°, ·794. It absorbs vapour of water, and becomes diluted by exposure to damp air; boils at 173° Fahr. It has never been frozen.

Alcohol distilled from Carbonate of Potash has a specific gravity of ·815 to ·823, and contains 90 to 93 per cent. of real spirit.

The specific gravity of ordinary rectified Spirits of Wine is about ·836, and it contains 80 to 83 per cent. of absolute Alcohol.

Different Commercial qualities of Alcohol.—Alcohol really absolute is not often used in Photography; the expense of making it is very great, and it could not be prepared at a profit. A spirit with less than four per cent. of water (sp. gr. ·805) may be obtained by agitating commercial Spirits of Wine first with Carbonate of Potash in the manner presently to be advised, and then with a common quality of dry Chloride of Calcium. Put in about three quarters of a pound of the Chloride of Calcium to half a gallon of Spirit of ·815; the greater part dissolves with perceptible rise of temperature. Draw over as much as possible in a steam bath; afterwards adding a little water to the residue in the retort to prevent it from setting into a hard mass as it cools. In this way the commercial absolute Alcohol is usually prepared.

The next quality of Spirit is the strong Alcohol of ·815 to ·823. This may be obtained by agitating Spirits of Wine, ·836, with an excess of dry Carbonate of Potash. The salt termed Carbonate of Potash is a *deliquescent* salt, having a great attraction for water; consequently when Spirit of Wine is shaken with Carbonate of Potash, a portion of water is removed, the salt dissolving in it and forming a dense liquid, which refuses to mix with the Alcohol, and sinks to the bottom. At the expiration of two or three days, if the bottle has been shaken frequently, the action is complete, and the lower stratum of fluid may be drawn off and rejected.

In order to obtain the greatest amount of concentration, it will be necessary to have a series of vessels, each containing about a pound of the Carbonate to a gallon of Spirit. The Alcohol may be passed from one to the other, and should not be distilled until the finely-powdered Carbonate can be shaken about in the liquid without being wetted. The Carbonate which the Writer employs is nearly pure, and costs from a shilling to eighteen-pence per pound; it must be dried on a hot metal plate before use. A commoner variety would answer, but it has the disadvantage of clotting together at the bottom of the vessel, and of not dissolving into a clear liquid.

A third quality of commercial Alcohol is the rectified Spirit of Wine of ·836 already referred to; it is very suitable for adding to developing fluids, etc., but not sufficiently strong for good Collodion.

Alcohol for Collodion Photography.—For a long time the Writer was in the habit of employing rectified Spirits of Wine for the preparation of Collodion, increasing its strength as far as necessary, by means of dry Carbonate of Potash; but having at length become dissatisfied with the smell of certain samples of this rectified Spirit, he has since used a strong Alcohol obtained by one distillation. In rectifying Spirit, a liquid known as "faints" is sometimes mixed with the purer Spirit for the sake of economy, and these faints are invariably contaminated with essential Oils. It is most important in Photography to avoid essential Oils, and therefore the grain Spirit obtained by one distillation in a Coffey's still may be preferred. In taking the specific gravity of this grain Spirit, which varies from ·817 o ·819 at 60° Fahr., we see at once the advantage likely o accrue from its employment, since the fusel Oil, which boils at a more elevated temperature, cannot rise so high n the still, and is separated. The smell of the grain Spirit s very sweet; and although it is not quite so strong as is equired, yet by converting a portion of it into Alcohol of 905, by means of dry Chloride of Calcium, and mixing his with the remainder, the correct specific gravity may asily be obtained.

The reaction to test-paper of the pure grain Spirit should be quite neutral; but in some instances a trace of acid is present, so that each half-gallon of Spirit requires about one drop of the standard solution of Ammonia alluded to at page 267. The Writer has never yet found in this or any other Spirit the alkaline reaction which is exhibited by Ether.

ALCOHOL (*Methylated*).

Spirit of Wine containing ten per cent. of Wood Naphtha is allowed by the excise laws to be sold free of duty, under the name of "Methylated Spirit." The quality however is often inferior, since residues containing fusel oil and other volatile bodies are usually rectified for the purpose of methylating.

ALCOHOL, METHYLIC.

This liquid, known also by the name of *Wood Naphtha* and *Pyroxylic Spirit,* is one of the products of the destructive distillation of woody fibre. It is volatile and limpid, with a pungent odour. In composition and properties it is allied to common Alcohol.

Commercial Naphtha is not by any means a pure substance, and requires a second rectification from Carbonated Alkali to remove water and brown colouring matter.

AMMONIA.

Symbol, NH_3 or NH_4O. Atomic weight, 17.

The liquid known by this name is an aqueous solution of the volatile gas Ammonia. Ammoniacal gas contains one atom of Nitrogen combined with three of Hydrogen: these two elementary bodies exhibit no affinity for each other, but they can be made to unite under certain circumstances, and the result is Ammonia.

Properties of Ammonia.—Ammoniacal gas is soluble in water to a large extent: the solution possessing those properties which are termed alkaline (p. 450). Ammonia however differs from the other alkalies in one important particular—it is volatile: hence the original colour of turmeric-paper affected by Ammonia is restored on the application of heat. Solution of Ammonia absorbs Carbonic Acid rapidly from the air, and is converted into Carbonate of Ammonia; it should therefore be preserved in stoppered bottles. Besides Carbonate, commercial Ammonia often contains Chloride of Ammonium, recognized by the white precipitate given by Nitrate of Silver after acidifying with pure Nitric Acid.

The strength of commercial Ammonia varies greatly; that sold for pharmaceutical purposes under the name of Liquor Ammoniæ, contains about ten per cent. of real Ammonia. The sp. gr. of aqueous Ammonia *diminishes* with the proportion of Ammonia present, the Liquor Ammoniæ being usually about ·936. It is a common error in Photographic operations to confound the diluted Ammonia with the Liquor Ammoniæ Fort., some samples of which are so strong that a single drop will neutralize a large portion of Acid.

Ammonia, although forming a large class of salts, appears at first sight to contrast strongly in composition with the alkalies proper, such as Potash and Soda. Mineral bases generally are *protoxides of metals*, as already shown at page 450, but Ammonia consists simply of Nitrogen and Hydrogen united without Oxygen. The following remarks may perhaps tend somewhat to elucidate the difficulty:—

Theory of Ammonium.—This theory supposes the existence of a substance possessing the properties of a *metal*, but differing from metallic bodies generally in being *compound* in structure: the formula assigned to it is NH_4, one atom of Nitrogen united with four of Hydrogen. This hypothetical metal is termed "Ammonium;" and Ammonia, associated with an atom of water, may be viewed as its *Oxide*, for $NH_3 + HO$ equals NH_4O. Thus, as Potash is the Oxide of *Potassium*, so Ammonia is the Oxide f *Ammonium*.

The composition of the *salts* of Ammonia is on this view assimilated to those of the alkalies proper. Thus Sulphate of Ammonia is a Sulphate of the Oxide of Ammonium; Muriate or Hydrochlorate of Ammonia is a Chloride of Ammonium, etc.

AMMONIA, CARBONATE OF.

This occurs commercially in lumps of a considerable size obtained by sublimation. Its composition is rather variable. When first formed it is probably a Sesquicarbonate, but by exposure to the air neutral Carbonate of Ammonia escapes, and a white powder is left which is a Bicarbonate.

AMMONIA, HYDROSULPHATE OF.

Symbol, $NH_4S\ HS$. Atomic weight, 51.

The liquid known by this name, and formed by passing Sulphuretted Hydrogen gas into Ammonia, is a double Sulphide of Hydrogen and Ammonium. In the preparation, the passage of the gas is to be continued until the solution gives no precipitate with Sulphate of Magnesia, and smells strongly of Hydrosulphuric Acid.

Properties.—Colourless at first, but afterwards changes to yellow, from liberation and subsequent solution of Sulphur. Becomes milky on the addition of any acid. Precipitates, in the form of Sulphide, all the metals which are affected by Sulphuretted Hydrogen, and, in addition, those of the class to which Iron, Zinc, and Manganese belong.

Hydrosulphate of Ammonia is employed in Photography to darken the Collodion image, and also as a test for the presence of Silver in certain solutions.

AMMONIA, NITRATE OF.

This is a neutral combination of Nitric Acid and Ammonia, which may be crystallized without difficulty. It is gradually formed in the Photographic Nitrate Bath when compounds of Ammonium are used in iodizing.

Nitrate of Ammonia is not of itself alkaline, but inasmuch as it is solvent of Oxide and also of Carbonate of Silver, a Bath containing Nitrate of Ammonia will give a strong Alkaline reaction on adding to it either Potash, Ammonia, or Chalk (p. 133).

AMMONIUM, BROMIDE OF.

Symbol, NH_4Br. Atomic Weight, 98.

This is a crystallized salt, which may be prepared by precipitating Bromide of Calcium by Carbonate of Ammonia. It is very soluble in water, and is more easily dissolved by Alcohol and Ether than the corresponding Bromide of Potassium. It does not become coloured on keeping, like the Iodide of Ammonium.

Bromide of Ammonium is a better form of Bromide for Collodion than the corresponding Salt of Potassium or Cadmium, and it can usually be obtained in a pure state.

AMMONIUM, CHLORIDE OF.

Symbol, NH_4Cl. Atomic weight, 53·5.

This salt, also known as Muriate or Hydrochlorate of Ammonia, occurs in commerce in the form of colourless and translucent masses, which are procured by *sublimation*, the dry salt being volatile when strongly heated. It dissolves in an equal weight of boiling, or in three parts of cold water. It contains more Chlorine in proportion to the weight used than Chloride of Sodium, the atomic weights of the two being as 53·5 to 58·5.

Chloride of Ammonium is easily obtained in a pure state, and is, on the whole, more suitable for salting paper than either Chloride of Sodium or Chloride of Barium.

AMMONIUM, IODIDE OF.

Symbol, NH_4I. Atomic weight, 145.

Properties.—Usually sold in small crystals, which have more or less of a yellow colour. An unstable substance and prone to liberation of Iodine, but may be kept for an unlimited length of time, if thoroughly dried and put away in a dark place. Very much more soluble in Alcohol than Iodide of Potassium, and not precipitated on adding Ether. Also soluble to a large extent in water: Alkaline reaction to litmus-paper.

Preparation.—In former editions the Writer has described a mode of preparing Iodide of Ammonium by dissolving Iodine in Hydrosulphate of Ammonia; but a more extended experience has shown him that traces of a Sulphur compound are often present in the Iodide made in that way. In order therefore to obtain an Ammonium compound equal to the Iodide of Potassium as regards sensitiveness in Collodion, he recommends that an Iodide of Calcium be first formed, and afterwards precipitated by Carbonate of Ammonia. This process is more troublesome than the last, but gives a very good result. Dry the crystals *in vacuo* over Sulphuric Acid.

Impurities.—Sulphate of Ammonia is often present to a large extent in commercial Iodide of Ammonium, and sometimes Carbonate of Ammonia, introduced for the purpose of preserving it in a colourless condition. Make a concentrated aqueous solution, and add a few drops of solution of Chloride of Barium. A white deposit indicates either Sulphate or Carbonate; but if the precipitate is at once taken up on dropping in one or two drops of Glacial Acetic Acid, it consists of Carbonate of Baryta. Sulphate of Ammonia is mostly left behind on dissolving the iodide in Alcohol of ·805, sold as absolute; but the Carbonate dissolves, and Collodion iodized with this solution, eventually renders the Bath alkaline by producing Carbonate of Silver.

To decolorize Iodide of Ammonium which has been decomposed by keeping, shake it up with a little Ether, pure or methylated; the Iodine will be dissolved out, and, unless Alcohol be present, no great loss from solution will result.

AQUA REGIA. *See* NITRO-HYDROCHLORIC ACID.

ARSENIC, BROMIDE OF.

Symbol, $AsBr_3$. Atomic weight, 315.

Bromide of Arsenic has been used in Collodion for the purpose of increasing the intensity of the developed image. A solution suitable for that purpose may be prepared by reducing Metallic Arsenic to a fine powder and placing it in a dry bottle with Alcohol of sp. gr. ·805. Bromine is then to be dropped into the Alcohol, when immediate combination will ensue; the Arsenic must always be in excess.

The addition of water decomposes Bromide of Arsenic, into Arsenious Acid and Hydrobromic Acid: hence the necessity for using Alcohol of considerable strength.

AURO-CHLORIDE OF SODIUM.

See SODIUM, AURO-CHLORIDE OF.

BARIUM, CHLORIDE OF.

Symbol, $BaCl + 2\ Aq$. Atomic weight, 122.

Barium is a metallic element very closely allied to Calcium, the elementary basis of *Lime.* The Chloride of Barium is commonly employed as a test for Sulphuric Acid, with which it forms an insoluble precipitate of Sulphate of Baryta. It also slightly alters the colour of the Photographic image when used in preparing Positive paper, which may be due, in some measure, to a chemical combination of Baryta with Albumen: but it must be remembered that this Chloride, from its high atomic weight, contains *less Chlorine* than the alkaline Chlorides.

Properties of Chloride of Barium.—Chloride of Barium occurs in the form of white crystals, soluble in about two parts of water, at common temperatures. These crystals contain two atoms of water of crystallization, which are expelled at 212°, leaving the anhydrous Chloride.

BARYTA, NITRATE OF.

Symbol, $BaO\ NO_5$. Atomic weight, 130·5.

Nitrate of Baryta forms octahedral crystals, which are anhydrous. It is considerably less soluble than the Chloride of Barium, requiring for solution twelve parts of cold and four of boiling water. It may be substituted for the Nitrate of Lead in the preparation of Protonitrate of Iron.

BENZOLE.

Symbol, $C_{12}H_6$.

A limpid liquid, obtained commercially by distilling off the most volatile constituent of the substance known as " Mineral Naphtha." It does not mix with water, but is dissolved in any quantity by Alcohol or Ether.

Benzole is an excellent solvent of fats and oils, and may be employed for removing grease-spots. It also dissolves Gutta-percha and Caoutchouc. A rapidly drying varnish may be made with Benzole, but it should first be purified by redistillation, since ordinary Benzole is apt to leave a greasy residue on drying.

BROMINE.

Symbol, Br. Atomic weight, 80.

This elementary substance is obtained from the uncrystallizable residuum of sea-water, termed *bittern*. It exists in the water in very minute proportion, combined with Magnesium in the form of a soluble Bromide of Magnesium.

Properties.—Bromine is a deep reddish-brown liquid of a disagreeable odour, and fuming strongly at common temperatures; sparingly soluble in water (1 part in 23, Löwig), but more abundantly so in Alcohol, and especially in Ether. It is very heavy, having a specific gravity of 3·0.

Bromine is closely analogous to Chlorine and Iodine in its chemical properties. It stands on the list intermediately between the two; its affinities being stronger than those of Iodine, but weaker than Chlorine (see Chlorine).

It forms a large class of salts, of which the Bromides of Potassium, Ammonium, Cadmium, and Silver are the most familiar to Photographers.

CADMIUM.

A white metal, resembling Tin in its physical properties. Its Oxide is found associated with Zinc in certain of the ores of the latter, but the two are easily separated.

The Iodide and Bromide of Cadmium are used in Photography, on account of their permanency and the facility with which they dissolve in Ether and Alcohol.

Metallic Cadmium is sometimes employed to remove free Iodine from Collodion.

CADMIUM, IODIDE OF.

Symbol, Cd I. Atomic weight, 183.

This salt is formed by heating filings of metallic Cadmium with Iodine, or by mixing the two with addition of water.

Iodide of Cadmium is very soluble, both in Alcohol and Water; the solution yielding on evaporation large six-sided tables of a pearly lustre, which are permanent in the air. The commercial Iodide is sometimes contaminated with Iodide of Zinc, the crystals being imperfectly formed and slowly liberating Iodine when dissolved in Ether and Alcohol. Pure Iodide of Cadmium remains nearly or quite colourless in Collodion, if the fluid be kept in a cool nd dark place.

CALCIUM, CHLORIDE OF.

Symbol, Ca Cl. Atomic weight, 55·5.

This salt is found in sea-water; but is usually prepared tificially by dissolving Chalk in Hydrochloric Acid and vaporating. When strongly dried, it occurs in lumps hich are hard and difficult to pulverize.

Chloride of Calcium has a great attraction for water, nd is used for drying gases and other purposes. Exposed the air, it soon deliquesces from absorption of atmoheric moisture. It is very soluble in Alcohol with evolution of heat, and when the liquid is subjected to distillation, a highly concentrated spirit passes over, leaving a viscid mass which crystallizes on cooling, and contains nearly sixty per cent. of Alcohol in a state of loose chemical combination with the Chloride.

Pure dry Chloride of Calcium is an expensive salt, but a common quality, sufficiently good for the use above described, may be obtained at a lower price.

CAMPHOR.

This substance is the produce of the *Laurus Camphora* of Japan and China. It occurs when pure in sublimed masses, which are tough and cannot be reduced to powder without the aid of a few drops of spirit. It evaporates slowly in the air at ordinary temperatures.

Camphor is soluble in Alcohol, but very sparingly indeed in water. Hence a piece of any size may be put into the liquid without fear of adding an excess.

CAOUTCHOUC.

This substance, known also as Indian-rubber, is the inspissated milky juice of trees growing in South America and the East Indies. It is insoluble in water and in Alcohol.

Chloroform is the most perfect solvent for Caoutchouc, and leaves it unchanged on evaporation. Benzole also acts upon it. Mineral Naphtha takes it up on applying heat, but the residue after evaporation is sticky.

When placed in contact with Sulphur, Caoutchouc undergoes a change of properties, familiar to us in the article sold as *vulcanized Indian-rubber*.

CASEINE. *See* MILK.

CELLULOSE.

This term is applied to the pure form of vegetable fibre existing in carefully bleached cotton, flax, etc. Cellulose, as before shown (p. 97), is the material which forms the cell-wall of the tissues of plants, and Lignine is the deposit formed in the interior of the cell. Hence the former is most abundant in the pith and newly-formed wood, whilst the latter is found in parts of older growth which have become hard and solid.

Many of the properties of Cellulose have been incidentally mentioned in this Work, such as its conversion into artificial parchment, Dextrine, Grape Sugar, etc., by Sulphuric Acid in particular states of dilution (p. 101), or into Pyroxyline or Xyloidine by the action of Nitric Acid (p. 100). The effect of dry distillation in decomposing it and producing Pyroxylic Spirit, Acetic Acid, and tarry matter, is alluded to in other parts of the Vocabulary.

A new solvent for Cellulose has lately been discovered, prepared by exposing copper turnings to the air in contact with Ammonia. The presence of a saline body like Nitrate of Ammonia prevents the Cellulose from being dissolved, and hence the ordinary blue liquid known as the Ammoniacal Oxide of Copper will not answer the purpose.

For further particulars as to the properties of Cellulose, see Art. " Cotton."

CHARCOAL, ANIMAL.

Animal Charcoal is obtained by heating animal substances, such as bones, dried blood, horns, etc., to redness, in close vessels, until all volatile empyreumatic matters have been driven off, and a residue of Carbon remains. When prepared from bones, it contains a large quantity of inorganic matter in the shape of Carbonate and Phosphate of Lime, the former of which produces *alkalinity* in reacting upon Nitrate of Silver (p. 133). Animal Charcoal is freed from these earthy salts by repeated digestion in Hydrochloric Acid; but unless very carefully washed it is apt to retain an acid reaction, and so to liberate free Nitric Acid when added to solution of Nitrate of Silver.

Properties.—Animal Charcoal, when pure, consists solely of Carbon, and burns away in the air without leaving any residue: it is remarkable for its property of decolorizing solutions; the organic colouring substance being separated, but not actually *destroyed*, as it is by Chlorine employed as a bleaching agent. This power of absorbing colouring matter is not possessed in an equal degree by all varieties of Charcoal, but is in great measure peculiar to those derived from the animal kingdom.

CHLORINE.

Symbol, Cl. Atomic weight, 35·5.

Chlorine is a chemical element, found abundantly in nature, combined with metallic Sodium in the form of Chloride of Sodium, or Sea-Salt.

Preparation.—By distilling common Salt with Sulphuric Acid, Sulphate of Soda and Hydrochloric Acid are formed. Hydrochloric Acid contains Chlorine combined with Hydrogen; by the action of *nascent* Oxygen (see Oxygen), the Hydrogen may be removed in the form of water, and the Chlorine left alone.

Properties.—Chlorine is a greenish-yellow gas, of a pungent and suffocating odour; soluble to a considerable extent in water, the solution possessing the odour and colour of the gas. It is nearly 2½ times as heavy as a corresponding bulk of atmospheric air.

Chemical properties.—Chlorine belongs to a small natural group of elements which contains also Bromine, Iodine, and Fluorine. They are characterized by having a strong affinity for Hydrogen, and also for the metals; but are comparatively indifferent to Oxygen. Many metallic substances actually undergo *combustion* when projected into an atmosphere of Chlorine, the union between the two taking place with extreme violence. The characteristic bleaching properties of Chlorine gas are explained in the same manner:—Hydrogen is removed from the organic substance, and in that way the structure is broken up and the colour destroyed.

Chlorine is more powerful in its affinities than either

Bromine or Iodine. The salts formed by these three elements are closely analogous in composition and often in properties. Those of the Alkalies, Alkaline Earths, and many of the Metals, are soluble in water: but the Silver salts are insoluble; the Lead salts sparingly so.

The combinations of Chlorine, Bromine, Iodine, and Fluorine, with Hydrogen, are acids, and neutralize Alkalies in the usual manner, with formation of Alkaline Chloride and water (p. 453).

The test by which the presence of Chlorine is detected, when free or in combination with bases, is *Nitrate of Silver*; it gives a white curdy precipitate of Chloride of Silver, insoluble in Nitric Acid, but soluble in Ammonia. The solution of Nitrate of Silver employed as the test must not contain Iodide of Silver, since this compound is precipitated by dilution.

CHLOROFORM.

Symbol, $C_2H\,Cl_3$.

This volatile liquid is obtained by the action of Chloride of Lime upon dilute Alcohol. It does not unite with water, but is very soluble in Spirit.

Chloroform is the best solvent known for Caoutchouc, and it also dissolves Gutta-percha readily. Amber and many other resins are more or less soluble in Chloroform; and hence this liquid will doubtless come into more general use as a material for rapidly drying varnishes, now that it can be supplied at a comparatively cheap rate, from the use of Methylated spirits in its manufacture.

CITRIC ACID.

This acid is found abundantly in lemon-juice and in lime-juice. It occurs in commerce in the form of large crystals, which are soluble in less than their own weight of water at 60°.

Commercial Citric Acid is sometimes mixed with Tartaric Acid. The adulteration may be discovered by making a concentrated solution of the acid and adding *Acetate of Potash:* crystals of Bitartrate of Potash will separate if Tartaric Acid be present.

A single atom of Citric Acid decomposes three atoms of Carbonate of Soda. One atom of Tartaric Acid however decomposes only *two* atoms of the Carbonate, so that if Citric Acid be adulterated with Tartaric Acid the alkali is in excess when the proportions given in the Photographic formulæ for making Citrates are adopted.

Citric Acid retards the reduction of Silver Salts by a developer, when the acid is present in a free state. But Citric Acid previously neutralized by an alkali acts as a reducing agent, and precipitates metallic Gold from a solution of Chloride of Gold.

COTTON.

The Cotton of commerce is obtained from three principal sources, America, India, and the South Sea Islands, but the largest supply comes from America. There is a considerable difference in the quality of Cotton as regards length of fibre, etc., and hence the market price of the raw material varies from fourpence halfpenny to fourteenpence per pound.

Rough Cotton as it is imported is not in a state to be used commercially; it must first be carefully combed and cleaned. Even the finest Cotton Wool, however, as it is prepared for the jeweller and for surgical purposes, may with advantage be further purified if required in making Photographic Pyroxyline. The fibre of the Cotton, as it exists in the pod, is encased by a film of oily or resinous matter, which, when the Cotton is immersed in Nitro-Sulphuric Acid of the correct strength for making soluble Pyroxyline, and at a temperature of 150° Fahr., resists for a time the action of the Nitric Acid, and much squeezing with the glass rod is required to wet the Cotton, and to make it imbibe the fluid: bubbles of air are entangled at first, and cannot easily be expelled, but almost immediately afterwards an evolution of red fumes takes place, and the fibre is destroyed by oxidation. On the other hand, with Cotton which has been previously treated with a diluted alkali so as to saponify the resin and remove it in a soluble form, there is no difficulty whatever in making it absorb the acid; it sucks up the liquid like a sponge, and remains during the whole time of the digestion without dissolving. From the finest qualities of Cotton Wool, traces of soluble matter are extracted by Potash, sufficient to impart a strong yellow colour to the alkaline liquid, and which, if permitted to remain, deoxidize that portion of the Nitric Acid immediately in contact with the fibre, and so far weaken it as to ensure the immediate solution of a part of the Cotton.

The Cotton which the Author of this Work has used for Pyroxyline, may be obtained of Messrs. Hutton and Co., 6, Newgate Street, City: it is the finest quality procurable, and is sold at two shillings per pound. This Cotton is of American growth, but not always from the same State, since it appears that the manufacturer, in making his purchases, is guided by the varying price of the market. It is sent out in packets of one pound each, which may be divided into quarters, and each quarter boiled gently for two hours, in a solution of two ounces of Potash (at two shillings and sixpence per pound) to a gallon of water. The mass is lifted out, and well squeezed, with repeated changes of water, for about twenty minutes, after which it is spread out to dry. It is important to remove the whole of the Potash, and to disturb the fibre of the Cotton as little as possible, since if it become knotted and twisted, the action of the Nitric Acid will be interfered with.

It may perhaps be suggested that the Potash is likely to exercise a chemical or modifying action on the fibre of the Cotton, but it does not appear to have any such effect when used in dilute solution. A somewhat stronger Potash has been stated to affect the cellulose by degrees, and to produce more or less of the condition which we see in old and rotten calico, as compared with the new material; but there need be no apprehension of this in the process above described, because Cotton fabrics which have been weakened by wear and repeated washings, become more easily soluble in Nitro-Sulphuric Acid, whereas the Cotton-wool, by boiling in weak alkali, is rendered less soluble in the Acids.

It has not at present been absolutely proved that all varieties of Cotton correspond as regards the solvent action of the weak Nitro-Sulphuric Acid, even when the cleansing has been correctly performed: the removal of the resinous impurity, however, is undoubtedly a point of importance.

ETHER.

Symbol, C_4H_5O. Atomic weight, 37.

Ether is obtained by distilling a mixture of Sulphuric Acid and Alcohol. If the formula of Alcohol ($C_4H_6O_2$) be compared with that of Ether, it will be seen to differ from it in the possession of an additional atom of Hydrogen and of Oxygen: in the reaction the Sulphuric Acid removes these elements in the form of *water*, and by so doing converts one atom of Alcohol into an atom of Ether. The term *Sulphuric* applied to the commercial Ether has reference only to the manner of its formation.

Properties of Ether.—Ether is a limpid and colourless fluid, with a peculiar and fragrant odour. Specific gravity, at 60°, about ·720. Boils at 98° Fahrenheit. The vapour is exceedingly dense, and may be seen passing off from the liquid and falling to the ground: hence the danger of pouring Ether from one bottle to another if a flame be near at hand.

Ether does not mix with water in all proportions; when the two are shaken together, after a short time the former rises and floats upon the surface. In this way a mixture of Ether and Alcohol may be purified to some extent, as in the common process of *washing* Ether. The water employed however always retains a certain portion of Ether (about a tenth part of its bulk), and acquires a strong ethereal odour; washed Ether also contains water in small quantity.

Bromine and Iodine are both soluble in Ether, and gradually react upon and decompose it. The strong alkalies, such as Potash and Soda, also decompose Ether slightly after a time, but not immediately. Nitric Acid oxidizes it with evolution of red fumes. Exposed to air and light, Ether is *ozonized* and acquires a peculiar odour (page 104): after a time Acetic Acid and Acetic Ether are formed by a further action of oxygen.

Ether dissolves fatty and resinous substances readily, but inorganic salts are mostly insoluble in this fluid. Hence Iodide of Potassium and other substances dissolved in Alcohol are precipitated to a certain extent by the addition of Ether.

Ether for Photographic use.—The preparation of pure Ether is of the utmost importance in Collodion Photography, since traces of foreign bodies, which analysis fails to detect, may produce an injurious effect. In the distillation of Ether, the crude product first obtained is contaminated with Oil of Wine, and contains foul-smelling organic bodies, from which it is partially freed by digestion with Lime or a caustic alkali; the object being to saponify the impurities and retain them in the body of the retort. It sometimes happens in this process that minute traces of the alkali are mechanically carried over by the Ether, and these are injurious to the keeping qualities of Collodion.

A quality of commercial Ether, having a sp. gr. of about 750 and answering to the demands of the Pharmacopœia, s much used for making Collodion. This Ether however ften leaves an unpleasant smell when allowed to evapoate in the hand, and hence the Writer for some time mployed in preference a stronger quality, sp. gr. ·728, btained by agitating the above with caustic alkali and rawing over the first portions only.

Even with these precautions however it was found diffiult to obtain a really uniform substance, for although the specific gravity was nearly the same, a perceptible difference in smell could be detected, and the keeping properties of the plain Collodion were found to vary. The following plan was therefore adopted and with manifest advantage, viz. to agitate the best Ether in a vessel containing water acidulated with Sulphuric Acid, and then to draw over the first half in a retort; in this way any traces of alkali are retained, and the impurities if present accumulate in the last portions.* The product appears invariably to restore the blue colour of reddened litmus-paper, and therefore this alkaline reaction is probably peculiar to Ether, although it has been stated in chemical works that Ether is neither acid nor alkaline.

The chemistry of the manufacture of Ether is not precisely understood. The Author has seen a sample of Ether so light that a test tube containing it nearly boiled when held in the hand, and yet this same sample injured the quality of all the Collodion to which it was added, changing the Negative picture into an image *positive* by transmitted light.

Ether prepared from Methylated Spirit (see Alcohol) is extensively employed in the manufacture of Collodion, and especially of Positive Collodion. Great exertions have been lately made to improve the quality of this material, but at one time it was so variable that two samples could scarcely be found to give corresponding results. The presence of the gaseous Methylic Ether introduces a difficulty, inasmuch as this substance is more prone to absorb Oxygen than pure Ether.

A test often applied to Ether is to agitate it with an equal bulk of strong Alcohol containing Iodide of Potassium dissolved in the proportion of 3½ grains to the ounce of spirit. The mixture should remain nearly or quite colourless for several days, when the thermometer is at

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* The remaining half of the Ether may after distillation be employed for Positive Collodion, or for Bromo-iodized Negative Collodion, in which the quality of the Ether is not of so much importance as in simply iodized Collodion.

60° Fahr. It is possible to make any Ether stand the test of Iodide of Potassium most perfectly, by agitating it with a little dry Carbonate of Potash; but the resulting Collodion would be injured rather than improved by such a process, since Carbonated Alkali decomposes Gun-Cotton. When, however, we obtain a sample of Ether which has been distilled from Sulphuric Acid, and yet find it to remain colourless for a long time on adding Iodide of Potassium, we may be assured of its perfect freedom from the "ozonized" principle.*

The difference between bad and good Ether is seen most evidently after long keeping. Supposing white light to be excluded, a pure sample of Ether may be placed in a bottle, only half full, and at the expiration of two or three months it will scarcely become coloured on the first addition of Iodide of Potassium. Ether only partially purified will often stand the test of Iodide of Potassium when freshly distilled, but it will soon acquire the property of liberating Iodine when it is stowed away for keeping. Thus, for instance, if traces of *aldehyde* be present in the Ether, this Aldehyde will gradually absorb Oxygen, and the Ether will deteriorate.

ETHER, ACETIC.

This compound Ether may be produced by distilling Acetate of Soda with Sulphuric Acid and Alcohol. It is a limpid liquid with a sweet and fragrant smell. It is also pontaneously formed in small quantities in ordinary Ether, or more especially in Ether containing dissolved Pyroxyline, its production being due to a slow process of oxidation. In a developing fluid or a Nitrate Bath containing both Acetic Acid and Alcohol, the peculiar smell of Acetic Ether is soon to be detected.

Acetic Ether is a powerful solvent for Pyroxyline, and eaves it on evaporation in the form of a white powder.

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* The condition of Ether known as "ozonized," is the same as that to hich the term "acid" is often applied; but in testing samples of Ether, we rely find them acid to test-paper.

Its presence in Collodion is very injurious, since it destroys the tenacity and transparency of the film.

ETHER, METHYLIC.

This Ether bears the same relation to Pyroxylic Alcohol or Wood Spirit, that ordinary Ether bears to Alcohol from wine. It is a gaseous substance, which dissolves to a certain extent in water, but more abundantly so in Alcohol or Ether.

"Methylated Ether," the peculiarities of which have been pointed out under the head of Ether, is made from a mixture of corn or wine spirit with ten per cent. of wood spirit (see "Alcohol, Methylated"). It must therefore contain a portion of gaseous Methylic Ether dissolved in an excess of common Ether.

GALLIC ACID.

Symbol, $C_7H_3O_5+Aq$. Atomic weight, 94.

The preparations and properties of Gallic Acid have been sufficiently described at page 27, to which the reader is referred. For the mode of preparing a saturated aqueous solution of Gallic Acid, and of preserving it from decomposition, see page 438.

GELATINE.

Symbol, $C_{13}H_{10}O_5N_2$.

This is an organic substance somewhat analogous to Albumen, but differing from it in properties. It is obtained by subjecting bones, hoofs, horns, calves' feet, etc., to the action of boiling water. The jelly formed on cooling is termed *size*, or, when dried and cut into slices, *glue*. Gelatine, as it is sold in the shops, is a pure form of Glue. *Isinglass* is gelatine prepared, chiefly in Russia, from the air-bladders of certain species of sturgeon.

Properties of Gelatine.—Gelatine softens and swells up in cold water, but does not *dissolve* until heated; the hot solution, on cooling, forms a tremulous jelly. One ounce of cold water will retain about three grains of Isinglass without gelatinizing; but much depends upon the temperature, a few degrees greatly affecting the result.

When long boiled in water, and especially in presence of an acid, such as the Sulphuric, Gelatine undergoes a peculiar modification, and the solution loses either partially or entirely its property of solidifying to a jelly.

The reactions of Gelatine with Nitrate of Silver have been described at pages 179 and 232.

GLYCERINE.

Fatty bodies are resolved by treatment with an alkali into an acid—which combines with the alkali, forming a *soap*,—and Glycerine, remaining in solution.

Pure Glycerine, as obtained by Price's patent process of distillation, is a viscid liquid of sp. gr. about 1·23; miscible in all proportions with water and Alcohol. It is peculiarly a neutral substance, exhibiting no tendency to combine with acids or bases. It has little or no action upon Nitrate of Silver in the dark, and reduces it very slowly even when exposed to light.

GLYCYRRHIZINE.

Glycyrrhizine, obtained from the fresh root of Liquorice, s a substance intermediate in properties between a sugar nd a resin. Sparingly soluble in water, but very soluble n Alcohol. It precipitates strong solution of Nitrate of ilver white, but the deposit becomes reddened by expoure to light.

A mode of preparing Glycyrrhizine has been described n which Carbonate of Potash is used, but the Author oes not find it to succeed. The process given in Miller's Elements of Chemistry' may however be depended on. rocure fresh Liquorice-root and slice it very fine *transersely*; then pound well in an iron mortar, and add as uch boiling water as will just cover it. Stand the jug a warm place for twelve hours, and afterwards press out the juice as far as possible by means of an iron screw-press. Evaporation by artificial heat is useless, and serves only to decompose the Glycyrrhizine.

Next mix Oil of Vitriol with an equal bulk of water and allow it to cool. Then add it to the strong infusion until test-paper becomes immediately red when dipped in the liquid, and a thick yellow deposit forms. A few drachms more or less of the Sulphuric Acid make but little difference, but if too much be used, the trouble of washing out the acid from the Glycyrrhizine will be increased.

Leave it for twelve hours, when the yellow deposit may be collected on a cloth. Begin by draining it nearly dry, and then wash it with a moderate quantity of water to remove the excess of Sulphuric Acid. Now squeeze it in a powerful press until it is dry enough to powder in the hand, and digest it without heat in Absolute Alcohol, about four or five times its weight. The pure Glycyrrhizine dissolves and a bulky mass of vegetable Albumen is left behind. Lastly, evaporate at a temperature not higher than 120° Fahr.

The only difficulty in the process is the washing of the impure Glycyrrhizine with water to remove the Sulphuric Acid, since the sugar is partially soluble in water, and even with proper care much of it is lost in the process. For this reason the Author thinks it better not to use too much acid in precipitating the Glycyrrhizine, although the quantity of deposit is greater when the acid is added freely.

The Glycyrrhizine exists in the root in combination with bases, Lime, etc., and is soluble in water, but insoluble in Alcohol. The Sulphuric Acid removes the bases, and the sugar-resin is then much more soluble in Alcohol than in Water. Alkalies and Alkaline Carbonates gradually decompose Glycyrrhizine, with production of a strong yellow colour.

GOLD, CHLORIDE OF.

Symbol, $AuCl_3$. Atomic weight, 303·1.

This salt is formed by dissolving pure metallic Gold in

Nitro-Hydrochloric Acid, and evaporating at a gentle heat. The solution affords deliquescent crystals of a deep orange colour.

Chloride of Gold, in a state fit for Photographic use, may easily be obtained by the following process:—Place a half-sovereign in any convenient vessel, and pour on it half a drachm of Nitric Acid mixed with two and a half drachms of Hydrochloric Acid and three drachms of water; digest by a gentle heat, but do not *boil* the acid, or much of the Chlorine will be driven off in the form of gas. At the expiration of a few hours add fresh Nitro-Hydrochloric Acid in quantity the same as at first, which will probably be sufficient, but if not, repeat the process a third time.* Next, dilute largely with distilled water, and add a filtered aqueous solution of common Sulphate of Iron (6 parts to 1 of Gold); collect the precipitated Gold, which is now free from copper; redissolve in Aqua Regia as at first, and evaporate to dryness on a water bath.

The weight of a half-sovereign is about 61 grains, of which 56 grains are pure gold. This is equivalent to 86 grains of Chloride of Gold, which will be the quantity contained in the solution.

Properties of Chloride of Gold.—As sold in commerce it usually contains excess of Hydrochloric Acid, and is then of a bright yellow colour; but when neutral and somewhat concentrated, it is dark red (*Leo ruber* of the alchemists). Chloride of Gold is decomposed with precipitation of metallic Gold by Charcoal, Sulphurous Acid, and many of the vegetable acids, such as Citric, Tartaric, etc.; also by Protosulphate and Protonitrate of Iron. It tinges the cuticle of an indelible purple tint. It is soluble in Alcohol and in Ether.

The most convenient mode of keeping the Chloride is in aqueous solution, one grain to the drachm of water. Sometimes a partial reduction of Gold will take place upon the sides of the bottle, but the quantity so deposited is very small, and may be disregarded.

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* Observe that if any *Silver* be present in the Gold coin it will produce a flocculent deposit of Chloride of Silver, thus preventing the solution from being complete.

GOLD, FULMINATING.

This is a yellowish-brown substance, precipitated on adding Ammonia to a strong solution of Chloride of Gold.

It may be dried carefully at 212°, but *explodes violently* on being heated suddenly to about 290°. Friction also causes it to explode when dry; but the moist powder may be rubbed or handled without danger. It is decomposed by Sulphuretted Hydrogen.

Fulminating Gold is probably an Aurate of Ammonia, containing two atoms of Ammonia to one atom of Peroxide of Gold.

GOLD, HYPOSULPHITE OF.

Symbol, $AuO\ S_2O_2$. Atomic weight, 252·6.

Hyposulphite of Gold is produced by the reaction of Chloride of Gold upon Hyposulphite of Soda (p. 192).

The salt sold in commerce as *Sel d'or* is a double Hyposulphite of Gold and Soda, containing one atom of the former salt to three of the latter, with four atoms of water of crystallization. It is formed by adding one part of Chloride of Gold, in solution, to three parts of Hyposulphite of Soda, and precipitating the resulting salt by Alcohol: the Chloride of Gold must be added to the Hyposulphite of Soda, and not the Soda Salt to the Gold.

Properties.—Hyposulphite of Gold is unstable and cannot exist in an isolated state, quickly passing into Sulphur, Sulphuric Acid, and metallic Gold. When combined with excess of Hyposulphite of Soda in the form of Sel d'or, it is more permanent.

Sel d'or occurs crystallized in fine needles, which are very soluble in water. The commercial article is often impure, containing little else than Hyposulphite of Soda, with a trace of Gold. It may be analyzed by adding a few drops of strong Nitric Acid (free from Chlorine), diluting with water, and afterwards collecting and igniting the yellow powder, which is metallic Gold.

GRAPE SUGAR.

Symbol, $C_{24}H_{28}O_{28}$.

This modification of Sugar, often termed *Granular Sugar*, or *Glucose*, exists abundantly in the juice of grapes and in many other varieties of fruit. It forms the saccharine concretion found in honey, raisins, dried figs, etc. It may be produced artificially by the action of fermenting principles and of dilute mineral acids, upon Starch.

Properties.—Grape Sugar crystallizes slowly and with difficulty from a concentrated aqueous solution, in small hemispherical nodules, which are hard, and feel gritty between the teeth. It is much less sweet to the taste than Cane Sugar, and is not so soluble in water (1 part dissolves in 1½ of cold water).

Grape Sugar tends to absorb Oxygen, and decomposes the salts of the noble metals, reducing them by degrees to the metallic state, even without the aid of light. *Cane* Sugar does not possess these properties to an equal extent, and hence it is readily distinguished from the other variety.

GUM ARABIC.

This substance is met with in the juices of many plants, but is found in its purest form in the transparent tears which exude from various species of Acacia.

Gum Arabic is now believed to consist of an organic substance resembling "mucilage," combined with a portion of Lime or other base. The mucilaginous constituent is not soluble in water, but simply swells up when wetted, without passing into solution: this body is present not only in Gum, but also in Linseed, Quince Seed, Marsh-Mallow Seed, etc. The addition of an alkali, or of an alkaline earth such as Lime, renders it more completely soluble in water, and thus diminishes the viscidity of the solution.

HONEY.

This substance contains two distinct kinds of Sugar, Grape Sugar, and an uncrystallizable substance analogous to, or identical with, the Treacle found associated with common Sugar in the cane-juice. The agreeable taste of Honey probably depends upon the latter, but its reducing power on metallic oxides is due to the former. Pure Grape Sugar can readily be obtained from inspissated Honey, by treating it with Alcohol, which dissolves out the syrup, but leaves the crystalline portion.

For Photographic use the Virgin Honey should be obtained direct from the comb, much of the commercial article being adulterated with flour, which causes it to ferment on the addition of water.

HYDROCHLORIC ACID.

Symbol, HCl. Atomic weight, 36·5.

Hydrochloric Acid is a volatile gas, which may be liberated from most of the salts termed Chlorides by the action of Sulphuric Acid. The acid, by its superior affinities, removes the base; thus,—

$$NaCl + HO\ SO_3 = NaO\ SO_3 + HCl.$$

Properties.—Abundantly soluble in water, forming the liquid Hydrochloric or Muriatic Acid of commerce. The most concentrated solution of Hydrochloric Acid has a sp. gr. 1·2, and contains about 40 per cent. of gas; that commonly sold is somewhat weaker, sp. gr. 1·14 to 1·16, containing about 28 per cent. real acid.

Pure Hydrochloric Acid is colourless, and fumes in the air. The yellow colour of the commercial acid depends upon the presence of traces of Perchloride of Iron, or of organic matter; commercial Muriatic Acid also often contains free Chlorine and Sulphuric Acid.

HYDRIODIC ACID.

Symbol, HI. Atomic weight, 128.

This is a gaseous compound of Hydrogen and Iodine, corresponding in composition to the Hydrochloric Acid. It cannot however, from its instability, be obtained in the same manner, since, on distilling an Iodide with Sulphuric Acid, the Hydriodic Acid first formed is subsequently decomposed into Iodine and Hydrogen. An aqueous solution of Hydriodic Acid is easily prepared by adding Iodine to water containing Sulphuretted Hydrogen gas; a decomposition takes place, and Sulphur is set free: thus, $HS + I = HI + S$.

Properties.—Hydriodic Acid is very soluble in water, yielding a strongly acid liquid. The solution, colourless at first, soon becomes brown from liberation of free Iodine. It may be restored to its original condition by adding solution of Sulphuretted Hydrogen.

HYDROSULPHURIC ACID.

Symbol, HS. Atomic weight, 17.

This substance, also known as Sulphuretted Hydrogen, is a gaseous compound of Sulphur and Hydrogen, analogous in composition to the Hydrochloric and Hydriodic Acid. It is usually prepared by the action of dilute Sulphuric Acid upon Sulphide of Iron, the decomposition being similar to that involved in the preparation of the Hydrogen Acids generally:—

$$FeS + HO\ SO_3 = FeO\ SO_3 + HS.$$

Properties.—Cold water absorbs three times its bulk of Hydrosulphuric Acid, and acquires the peculiar putrid odour and poisonous qualities of the gas. The solution is faintly acid to test-paper, and becomes opalescent on keeping, from gradual separation of Sulphur. It is decomposed by Nitric Acid, and also by Chlorine and Iodine. It precipitates Silver from its solutions in the form of black Sulphide of Silver; also Copper, Mercury, Lead, etc.; but Iron and other metals of that class are not affected, in presence of free acid. Hydrosulphuric Acid is constantly employed in the chemical laboratory for these and other purposes.

ICELAND MOSS.

Cetraria Islandica.—A species of Lichen found in Iceland and the mountainous parts of Europe; when boiled in water, it first swells up, and then yields a substance which gelatinizes on cooling.

It contains Lichen Starch, a bitter principle soluble in Alcohol, termed "Cetrarine," and common Starch; traces of Gallic Acid and Bitartrate of Potash are also present.

IODINE.

Symbol, I. Atomic weight, 127.

Iodine is chiefly prepared at Glasgow, from *kelp*, which is the fused ash obtained on burning seaweeds. The waters of the ocean contain minute quantities of the Iodides of Sodium and Magnesium, which are separated and stored up by the growing tissues of the marine plant.

In the preparation, the mother-liquor of kelp is evaporated to dryness and distilled with Sulphuric Acid; the Hydriodic Acid first liberated is decomposed by the high temperature, and fumes of Iodine condense in the form of opaque crystals.

Properties.—Iodine has a bluish-black colour and metallic lustre: it stains the skin yellow, and has a pungent smell, like diluted Chlorine. It is extremely volatile when moist, boils at 350°, and produces dense violet-coloured fumes, which condense in brilliant plates. Specific gravity 4·946. Iodine is very sparingly soluble in water, 1 part requiring 7000 parts for perfect solution: even this minute quantity however tinges the liquid of a brown colour. Alcohol and Ether dissolve it more abundantly, forming dark-brown solutions. Iodine also dissolves freely in solutions of the alkaline Iodides, such as the Iodide of Potassium, of Sodium, and of Ammonium.

Chemical Properties.—Iodine belongs to the Chlorine group of elements, characterized by forming acids with Hydrogen, and combining extensively with the metals (see

Chlorine). They are however comparatively indifferent to Oxygen, and also to each other. The Iodides of the alkalies and alkaline earths are soluble in water; also those of Iron, Zinc, Cadmium, etc. The Iodides of Lead, Silver, and Mercury are nearly or quite insoluble.

Iodine possesses the property of forming a compound of a deep blue colour with Starch. In using this as a test, it is necessary first to liberate the Iodine (if in combination) by means of Chlorine, or of Nitric Acid saturated with Peroxide of Nitrogen. The presence of Alcohol or Ether interferes to a certain extent with the result.

IODOFORM.

The composition of this substance is analogous to that of Chloroform, Iodine being substituted for Chlorine. It is obtained on boiling together Iodine, Carbonate of Potash, and Alcohol.

Iodoform occurs in yellow nacreous crystals, which have a saffron-like odour. It is insoluble in water, but soluble in spirit.

IRON, ACETATE OF.

There are two Acetates of Iron, a Protacetate, which is nearly colourless, and corresponds in properties and composition to the Protosalts of Iron, and a Peracetate, which is red, and resembles the Persalts of Iron.

A solution of the Protacetate containing a slight excess of the Sulphate, but sufficiently pure for Photographic purposes, may be made by dissolving 12 grains of Protosulphate of Iron and 12 grains of crystallized Acetate of Lead, each in half an ounce of water, mixing, and filtering from the white deposit, which is Sulphate of Lead. The solution is very unstable, and soon deposits a reddish Subsalt, or if Acetic Acid be present, it assumes a red colour.

A mixture of Acetate of Soda with Protosulphate of Iron, six grains of the former and twelve grains of the latter to an ounce of water, acts in Photography very much in the same manner as the pure solution of the Acetate.

IRON, AMMONIO-CITRATE OF.

This beautiful Pharmaceutical preparation, occurring in crystalline plates, is a salt containing Citric Acid in union both with Ammonia and with Peroxide of Iron.

The reaction of certain tests upon the Ammonio-Citrate and also upon the Ammonio-Tartrate of Iron, is peculiar. Free Ammonia, which usually throws down a red Sesquioxide from the Persalts of Iron, produces no deposit with these compounds; and Ferrocyanide of Potassium, which ought to precipitate Prussian blue, simply produces a purple colour. The presence of the vegetable acid appears to be the cause of these anomalies.

IRON, CHLORIDE OF.

Symbol, Fe_2Cl_3. Atomic weight, 162·5.

There are two Chlorides of Iron, corresponding in composition to the Protoxide and the Sesquioxide respectively. The Protochloride is very soluble in water, forming a green solution, which precipitates a dirty-white Protoxide on the addition of an alkali. The Perchloride, or the other hand, is dark brown, and gives a foxy-red precipitate with alkalies.

Properties.—Perchloride of Iron may be obtained in the solid form by heating Iron wire in excess of Chlorine; it condenses in the shape of brilliant and iridescent brown crystals, which are volatile, and dissolve in water, the solution being acid to test-paper. It is also soluble in Alcohol, forming the Tinctura Ferri Sesquichloridi of the Pharmacopœia. Commercial Perchloride of Iron ordinarily contains an excess of Hydrochloric Acid.

IRON, IODIDE OF.

Symbol, FeI. Atomic weight, 155.

Iodide of Iron is prepared by digesting an excess of Iron filings with pulverized Iodine and water. It is very soluble in water and in Alcohol, but the solution rapidly absorbs oxygen, and deposits Peroxide of Iron; hence the importance of preserving it in contact with metallic Iron, with which the separated Iodine may recombine. By very careful evaporation, hydrated crystals of Proto-iodide may be obtained, but the composition of the solid salt usually sold under that name cannot be depended on.

The *Periodide* of Iron, corresponding to the *Perchloride,* has not been examined, and it is doubtful whether any such compound exists.

IRON, PROTONITRATE OF.

Symbol, $FeO\ NO_5+7\ Aq$. Atomic weight, 153.

This salt, by careful evaporation *in vacuo* over Sulphuric Acid, forms transparent crystals, of a light green colour, and containing 7 atoms of water, like the Protosulphate. It is exceedingly unstable, and soon becomes red from decomposition, unless preserved out of contact with air. The preparation of solution of Protonitrate of Iron for developing Collodion Positives, is given at page 281.

IRON, PROTOSULPHATE OF.

Symbol, $FeO\ SO_3+7\ Aq$. Atomic weight, 139.

The properties of this salt, and of the two salifiable Oxides of Iron, are described at page 30. It dissolves in rather more than an equal weight of cold water, or in less of boiling water.

Aqueous solution of Sulphate of Iron absorbs the *Binoxide of Nitrogen,* acquiring a deep olive-brown colour; as this gaseous Binoxide is itself a reducing agent, the liquid so formed has been proposed as a more energetic developer than the Sulphate of Iron alone.

KAOLIN, OR CHINA CLAY.

This is prepared, by careful levigation, from mouldering granite and other disintegrated felspathic rocks. It is a *Silicate of Alumina,* containing Silicic Acid or *Flint,* united with the base Alumina. Kaolin is perfectly insoluble in water and in acids, and produces no decomposition in solution of Nitrate of Silver. It is employed by Photographers to decolorize solutions of Nitrate of Silver which have become brown from the action of Albumen or other organic matters.

Commercial Kaolin may contain chalk, in which state it produces alkalinity in solution of Nitrate of Silver. The impurity, detected by its effervescence with acids, is removed by washing the Kaolin in diluted vinegar and subsequently in water.

LEAD, ACETATE OF.

Symbol, $PbO\ AcO_3 + 3\ Aq$. Atomic weight, 189·6.

The neutral Acetate of Lead is a very abundant substance in commerce, and is known as *Sugar of Lead.* It is prepared by digesting Oxide of Lead in Pyroligneous or Acetic Acid; and crystallizes in acicular masses.

Acetate of Lead is easily soluble in cold water, but the solution is usually milky, either from the presence of a little Carbonate mixed with the Acetate, or from Carbonic Acid or Carbonate of Lime in the water used. The crystals employed in Pharmacy and sold at a low price are usually pure enough for Photographic purposes.

LEAD, NITRATE OF.

Symbol, $PbO\ NO_5$. Atomic weight, 165·6.

Nitrate of Lead is obtained by dissolving the metal, or the Oxide of Lead, in *excess* of Nitric Acid, diluted with 2 parts of water. It crystallizes on evaporation in white anhydrous tetrahedra and octahedra, which are hard, and decrepitate on being heated; they are soluble in 8 parts of water at 60°.

Nitrate of Lead forms with Sulphuric Acid, or with soluble Sulphates, a white precipitate, which is the insoluble Sulphate of Lead. The *Iodide* of Lead is also very sparingly soluble in water.

LIGNINE. *See* CELLULOSE.

LITHIUM, IODIDE OF.

Symbol, LI + 6 Aq. Atomic weight, 188.

Lithium is a rare substance, found in the mineral kingdom, and the reactions of its Oxide are so strong that it takes its place with the alkalies Potash and Soda. Metallic Lithium is the lightest solid body known, its density being little more than one-half of that of water.

Iodide of Lithium has been proposed for Photographic use, being more easily soluble in Alcohol than Iodide of Potassium. Its deliquescent nature however is an objection, as also is the difficulty and expense of obtaining it commercially in a pure state. A solution of the Iodide may be prepared by mixing equivalent proportions of crysallized Sulphate of Lithia and Iodide of Calcium in conentrated aqueous solution, evaporating to dryness over Sulphuric Acid *in vacuo*, and exhausting the dry residue with Alcohol of ·805. Iodide of Calcium is preferable to Iodide of Barium, in consequence of the latter being more frequently contaminated with an excess of base.

LITMUS.

Litmus is a vegetable substance prepared from various *chens*, which are principally collected on rocks adjoining he sea. The colouring matter is extracted by a peculiar rocess, and is afterwards made up into a paste with chalk, laster of Paris, etc.

Litmus occurs in commerce in the form of small cubes a fine violet colour. In using it for the preparation of st-papers, it is digested in hot water, the solution evaporated at a gentle heat, and sheets of porous paper soaked the blue liquid so formed. The red papers are prepared first in the same manner, but are afterwards placed in ater which has been rendered faintly acid with Sulphu or Hydrochloric Acid.

MAGNESIUM, IODIDE OF.

Symbol, $MgI + Aq$?

This Iodide has been recommended for Collodion in consequence of its ready solubility in Alcohol. Commercial Iodide of Magnesium usually contains free Iodine in some quantity, but a colourless solution of the Iodide sufficiently pure for Photographic use may easily be obtained as follows:—Take crystallized Sulphate of Magnesia and heat it in a porcelain capsule on a sand bath, until all the water of crystallization has been expelled, and a dry white mass remains. Pulverize twenty-five grains of this substance very finely, and rub it up in a glass mortar with thirty-two grains of pure Iodide of Potassium, likewise finely powdered. Then introduce it into a dry bottle with two fluid ounces of Alcohol of ·805, sold as absolute, and agitate for ten minutes or a quarter of an hour. Filter out the insoluble Sulphate of Potash and the excess of Sulphate of Magnesia, when the solution will be fit for use; it must be added in the usual proportion, viz. two drachms of the iodizing liquid to six of plain Collodion.

MERCURY, CHLORIDE OF
(formerly BICHLORIDE).

Symbol, $HgCl$. Atomic weight, 135·5.

This salt, also called Corrosive Sublimate, and often *Bichloride of Mercury* (the atomic weight of Mercury being doubled), may be formed by heating Mercury in excess of Chlorine, or, more economically, by subliming a mixture of Sulphate of Mercury and Chloride of Sodium.

Properties.—A very corrosive and poisonous salt, usually sold in semi-transparent, crystalline masses, or in the state of powder. Soluble in 16 parts of cold, and in 3 of hot water; more abundantly so in Alcohol, and also in Ether. The solubility in water may be increased by the addition of free Hydrochloric Acid, or of Chloride of Ammonium.

The Subchloride of Mercury is an insoluble white powder, commonly known under the name of *Calomel.*

MILK.

The Milk of herbivorous animals contains three principal constituents—Fatty matter, Caseine, and Sugar; in addition to these, small quantities of the Chloride of Potassium, and of Phosphates of Lime and Magnesia, are present.

The fatty matter is contained in small cells, and forms the greater part of the cream which rises to the surface of the milk on standing; hence *skimmed* milk is to be preferred for Photographic use.

The second constituent, *Caseine,* is an organic principle somewhat analogous to Albumen in composition and properties. Its aqueous solution however does not, like Albumen, coagulate on boiling, unless *an acid* be present, which probably removes a small portion of alkali previously in combination with the Caseine. The substance termed "rennet," which is the dried stomach of the calf, possesses the property of coagulating Caseine, but the exact mode of its action is unknown. Sherry wine is also commonly employed to curdle Milk; but brandy and other spirituous liquids, when free from acid and astringent matter, have no effect.

In all these cases a portion of the Caseine usually remains in a soluble form in the *whey;* but when the Milk is coagulated by the addition of acids, the quantity so left is very small, and hence the use of the rennet is to be preferred, since the presence of Caseine facilitates the reduction of the sensitive Silver salts by light.

Caseine combines with Oxide of Silver in the same manner as Albumen, forming a white coagulum, which becomes *brick-red* on exposure to light.

Sugar of Milk, the third principal constituent, differs from both cane and grape sugar; it may be obtained by evaporating *whey* until crystallization begins to take place. It is hard and gritty, and only slightly sweet; slowly soluble, without forming a syrup, in about two and a half parts of boiling, and six of cold water. It does not ferment and form Alcohol on the addition of yeast, like grape sugar, but by the action of *decomposing animal matter* is converted into Lactic Acid.

When skimmed Milk is exposed to the air for some hours, it gradually becomes *sour*, from Lactic Acid formed in this way; and if then heated to ebullition, the Caseine coagulates very perfectly.

NAPHTHA.

This name is applied to several liquids sold in commerce. First, *Wood Naphtha*, often used for burning in lamps, which is the same as Pyroxylic Spirit or Methylic Alcohol, *q. v.* Second, *Coal Naphtha*, a volatile liquid which distils over in the process of manufacturing gas; and, thirdly, *Mineral Naphtha*, found in the soil of certain parts of Italy, and a product of volcanic distillation.

The two latter substances, to which the name of Naphtha ought to be restricted, possess the same leading characters, and contain several Hydrocarbons, of which Benzole, extracted from Coal Naphtha, is a principal one.

Naphtha is not miscible with water, but dissolves in absolute Alcohol, Ether, and Oils. It is a solvent of bitumen, resins, etc., and is largely employed in liquefying Caoutchouc for the preparation of waterproof cloth.

NITRIC ACID.

Symbol, NO_5. Atomic weight, 54.

Nitric Acid, or *Aqua-fortis*, is prepared by adding Sulphuric Acid to Nitrate of Potash, and distilling the mixture in a retort. Sulphate of Potash and free Nitric Acid are formed, the latter of which, being volatile, distils over in combination with one atom of water previously united with the Sulphuric Acid.

Properties.—Anhydrous Nitric Acid is a solid substance, white and crystalline, but it cannot be prepared except by an expensive and complicated process.

The concentrated *liquid* Nitric Acid contains 1 atom of water, and has a sp. gr. of about 1·5; if perfectly pure, it is colourless, but usually it has a slight yellow tint, from partial decomposition into Peroxide of Nitrogen: it fumes strongly in the air.

The strength of commercial Nitric Acid is subject to much variation. An acid of sp. gr. 1·42, containing about 4 atoms of water, is often met with. If the specific gravity is much lower than this (less than 1·36), it will scarcely be adapted for the preparation of Pyroxyline. The yellow *Nitrous Acid*, so called, is a strong Nitric Acid partially saturated with the brown vapours of Peroxide of Nitrogen: it has a high specific gravity, usually about 1·45, but this is somewhat deceptive, being caused in part by the presence of the Peroxide. On mixing with Sulphuric Acid, the colour disappears, a compound being formed which has been termed a *Sulphate of Nitrous Acid.*

In the Appendix a Table is given which exhibits the quantity of real anhydrous Nitric Acid contained in samples of different densities.

Nitric Acid is a powerful oxidizing agent (see page 12); it dissolves all the common metals, with the exception of Gold and Platinum. Animal substances, such as the cu- icle, nails, etc., are tinged of a permanent yellow colour, nd are deeply corroded by a prolonged application. Ni- ric Acid forms a numerous class of salts, *all of which are oluble in water:* hence its presence cannot be determined y any precipitating reagent, in the same manner as that f Hydrochloric and Sulphuric Acid.

The principal impurities in commercial Nitric Acid are *hlorine and Sulphuric Acid;* also Peroxide of Nitrogen, hich tinges the acid yellow, as already described. Chlo- ine is detected by diluting the acid with an equal bulk of istilled water, and adding a few drops of Nitrate of Silver, —*a milkiness,* which is Chloride of Silver in suspension, dicates the presence of Chlorine. In testing for Sulphu- c Acid, dilute the Nitric Acid as before, and drop in *a ngle drop* of solution of Chloride of Barium; if Sulphuric Acid be present, an insoluble precipitate of Sulphate of Baryta will be formed.

Nitric Acid for Photographic use.—A convenient form of acid for preparing Pyroxyline is the Nitric Acid of 1·45. The question has been asked, why so concentrated an acid is recommended, seeing that it is afterwards to be diluted with water? There are two reasons; first, because this acid is cheaper after the rate, and perhaps more uniform than a weaker acid; and secondly, it is important that both the Sulphuric and Nitric Acid should be as strong as possible, in order to allow of the use of sufficient water to raise the temperature of the resulting Nitro-Sulphuric Acid at once to the proper point, and so to obviate the necessity of employing artificial heat.

A saving of expense is effected by using the yellow acid sold in commerce as "Acid Nitros," in place of the pure acid of equal strength; and for some time the Writer was of opinion that this might be done with impunity; it subsequently appeared, however, that the quantity of Chlorine in the "Nitros Acid" was more variable than had been supposed, and that it must necessarily remain so, inasmuch as the cargoes of Nitrate of Soda, from which the acid is made, differ in quality, and no preliminary process of purification is resorted to, with a view of eliminating the Chloride. The effect of Chlorine, when present in the Nitric Acid in more than a certain proportion, is to decompose the Pyroxyline, and to cause its partial solution in the Nitro-Sulphuric Acid: hence it becomes necessary to work with a smaller quantity of water, and consequently an inferior Pyroxyline is obtained.

NITRO-GLUCOSE.

When 3 fluid ounces of cold Nitro-Sulphuric Acid, consisting of 2 ounces of Oil of Vitriol and 1 ounce of highly concentrated Nitric Acid, are mixed with 1 ounce of finely powdered Cane Sugar, there is formed at first a thin, transparent, pasty mass. If it is stirred with a glass rod for a few minutes without interruption, the paste coagulates as it were, and separates from the liquid as a thick tenacious mass, aggregating into lumps, which can easily be removed from the acid mixture.

This substance has a very acid and intensely bitter taste. Kneaded in warm water until the latter no longer reddens litmus-paper, it acquires a silvery colour and a beautiful silky lustre. When dissolved in Collodion it *ozonizes* the Ether on keeping for some months, and hence there is a rapid liberation of Iodine when the iodizer is added. Alkalies decompose Nitro-Glucose, evolving a smell of burnt sugar. The product lessens the sensitiveness of Collodion, but increases the intensity of the image.

NITRO-HYDROCHLORIC ACID.

Symbol, NO_4+Cl.

This liquid is the Aqua Regia of the old alchemists. It is produced by mixing Nitric and Hydrochloric Acid: the Oxygen of the former combines with the Hydrogen of the latter, forming water and liberating Chlorine.

$$NO_5 + HCl = NO_4 + HO + Cl.$$

The presence of free Chlorine confers on the mixture the power of dissolving Gold and Platinum, which neither of the two acids possesses separately. In preparing Aqua Regia it is usual to mix one part, by measure, of Nitric Acid with four of Hydrochloric Acid, and to dilute with an equal bulk of water. The application of a gentle heat assists the solution of the metal; but if the temperature rises to the boiling point, effervescence and escape of Chlorine take place.

NITRO-SULPHURIC ACID.

This name is applied to a mixture of Nitric and Sulphuric Acid, the properties and preparation of which are described at page 98.

ORGANIC MATTER.

This term is often loosely employed to designate certain varieties of vegetable and animal substances which have no definite composition, and are prone to change by absorption of Oxygen. In illustration may be mentioned—Extracts, decayed woody fibre, mucilaginous and gummy substances, etc. Bodies which have a definite formula, however, are often included in the class of "Organic matters" if they easily pass by oxidation into ill-defined products. Thus, the Sugar of Liquorice, which soon decomposes and becomes brown, may be referred to under that head: but a stable vegetable acid like Acetic Acid, or a neutral substance not readily oxidizable, such as Glycerine, although really organic in composition, would not be correctly included in the same class.

Organic matter of the kind above alluded to reacts upon Nitrate of Silver in presence of light, reducing it more or less perfectly to the metallic state and becoming itself oxidized.

OXYGEN.

Symbol, O. Atomic weight, 8.

Oxygen gas may be obtained by heating Nitrate of Potash to redness, but in this case it is contaminated with a portion of Nitrogen. The salt termed Chlorate of Potash (the composition of which is closely analogous to that of the Nitrate, Chlorine being substituted for Nitrogen) yields abundance of pure Oxygen gas on the application of heat, leaving behind Chloride of Potassium.

Chemical Properties.—Oxygen combines readily with many of the chemical elements, forming Oxides. This chemical affinity however is not well seen when the elementary body is exposed the action of Oxygen *in the gaseous form.* Oxygen in its *nascent* state acts more powerfully as an oxidizer. By nascent Oxygen is meant Oxygen on the point of separation from other elementary atoms with which it was previously associated; it may then be considered to be in the liquid form, and hence it comes more perfectly into contact with the particles of the body to be oxidized.

Illustrations of the superior chemical energy of nascent over gaseous Oxygen are numerous, but none perhaps are more striking than the gradual oxidizing influence exerted by atmospheric air, as compared with the violent action of Nitric Acid and bodies of that class which contain Oxygen loosely combined.

OXYMEL.

This syrup of Honey and Vinegar is prepared as follows. Take of

Honey	1 pound.
Acid, Acetic, fortiss. (Beaufoy's Acid)	11 drachms.
Water	13 drachms.

Stand the pot containing the Honey in boiling water until a scum rises to the surface, which is to be removed two or three times. Then add the Acetic Acid and the water, and skim once more if required. Allow to cool, and it will be fit for use.

POTASH.

Symbol, $KO+H\dot{O}$. Atomic weight, 56.

Potash is obtained by separating the Carbonic Acid from Carbonate of Potash by means of Caustic Lime. Lime is a more feeble base than Potash, but the Carbonate of Lime, being *insoluble* in water, is at once formed on adding Milk of Lime to a solution of Carbonate of Potash (p. 456).

Properties.—Usually met with in the form of solid lumps, or in cylindrical sticks, which are formed by melting the Potash and running it into a mould. It always contains one atom of water, which cannot be driven off by the application of heat.

Potash is soluble almost to any extent in water, much heat being evolved. The solution is powerfully alkaline (p. 449), and acts rapidly upon the skin; it dissolves fatty and resinous bodies, converting them into soaps.

Solution of Potash absorbs Carbonic Acid quickly from the air, and should therefore be preserved in stoppered bottles; the glass stoppers must be wiped occasionally, in order to prevent them from becoming immovably fixed by the solvent action of the Potash upon the Silica of the glass.

The Liquor Potassæ of the London Pharmacopœia has a sp. gr. of 1·063, and contains about 5 per cent. of real Potash. It is usually contaminated with *Carbonate* of Potash, which causes it to effervesce on the addition of acids; also, to a less extent, with Sulphate of Potash, Chloride of Potassium, Silica, etc.

POTASH, BICHROMATE OF.

Symbol, $KO, 2\ CrO_3$. Atomic weight, 147·5.

This salt is largely manufactured at Glasgow for the use of the calico printers, from a native Chrom*ite* oxidized by Nitric Acid into a Chrom*ate*. It occurs in fine orange-coloured crystals, which are soluble in about ten parts of water at 60° Fahrenheit.

There are two Chromates of Potash,—a neutral Chromate, which is yellow and contains an atom of each constituent; and a Bichromate, nearly red, as before mentioned, and having two atoms of acid to one of base.

POTASH, CARBONATE OF.

Symbol, $KO\ CO_2$. Atomic weight, 69.

The impure Carbonate of Potash, termed *Pearlash*, is obtained from the ashes of wood and vegetable matter, in the same manner as Carbonate of Soda is prepared from the ashes of seaweeds. Salts of Potash and of Soda appear essential to vegetation, and are absorbed and appropriated by the living tissues of the plant. They exist in the vegetable structure combined with organic acids in the form of salts, Oxalate, Tartrate, etc., which when burned are converted into Carbonate.

Properties.—The Pearlash of commerce contains large and variable quantities of Chloride of Potassium, Sulphate of Potash, etc. A purer Carbonate is sold, which is free from Sulphates, and with only a trace of Chlorides. Carbonate of Potash is a strongly alkaline salt, deliquescent, and soluble in twice its weight of cold water; insoluble in Alcohol, and employed to deprive it of water.

POTASH, NITRATE OF.

Symbol, $KO\ NO_5$. Atomic weight, 101.

This salt, also termed *Nitre*, or *Saltpetre*, is an abundant natural product, found effloresced upon the soil in certain parts of the East Indies. It is also produced artificially in what are called Nitre-beds.

There are different qualities of Nitre sold in commerce, some of which contain much Chloride of Potassium, detected on dissolving the Nitre in distilled water and adding a drop or two of solution of Nitrate of Silver. This impurity is injurious when the Nitre is employed for Photographic use: in the manufacture of Pyroxyline it decomposes the Nitric Acid; and in the case of positive developing solutions, the presence of Chloride in the Nitre produces a white cloudiness on the film.

A quality of Nitre which answers very well for making Pyroxyline can be obtained at the operative chemist's, at one shilling per pound; it is often sold as pure Nitre, but usually contains sufficient Chloride to produce an opalescence with Nitrate of Silver; if the impurity is in larger quantity, and produces a decided precipitate with Nitrate of Silver, the sample must be rejected.

POTASH AND SODA, TARTRATE OF.

Formula, $KO, NaO, C_8H_4O_{10}+8\ Aq$.

This substance is often sold in commerce under the name of Rochelle Salt. It is prepared by adding Soda to the Bitartrate of Potash, and forms large crystals, having the appearance of six-sided prisms, perfect only on one side.

POTASSIUM, BROMIDE OF.

Symbol, KBr. Atomic weight, 119.

Bromide of Potassium is prepared by adding Bromine to Caustic Potash, and heating the product, which is a mixture of Bromide of Potassium and Bromate of Potash, to redness, in order to drive off the Oxygen from the latter salt. It crystallizes in anhydrous cubes, like the Chloride and Iodide of Potassium; it is easily soluble in water, but very sparingly so in Alcohol; it yields red fumes of Bromine when acted upon by Sulphuric Acid.

This salt is useful in Photographic processes on paper, but in Collodion it is liable to cause turbidity and spots.

POTASSIUM, CYANIDE OF.

Symbol, K, C_2N, or KCy. Atomic weight, 65.

This salt is a compound of Cyanogen gas with the metal Potassium. Cyanogen is not an elementary body, like Chlorine or Iodine, but consists of Carbon and Nitrogen united in a peculiar manner. Although a compound substance, it reacts in the manner of an element, and is therefore (like *Ammonium*, previously described) an exception to the usual laws of chemistry. Many other bodies of a similar character are known.

Properties.—These have been sufficiently described at page 58, to which the reader is referred. Carbonate of Potash is the principal impurity, but it does not produce any injurious effect beyond lessening the available strength in fixing; and hence it is a useless expense to attempt the purification of the salt by crystallizing it from Alcohol.

POTASSIUM, FLUORIDE OF.

Symbol, KF. Atomic weight, 58.

Preparation.—Fluoride of Potassium is formed by saturating Hydrofluoric Acid with Potash, and evaporating to dryness in a platinum vessel. *Hydrofluoric Acid* contains Fluorine combined with Hydrogen; it is a powerfully acid and corrosive liquid, formed by decomposing Fluor Spar, which is a *Fluoride of Calcium,* with strong Sulphuric Acid; the action which takes place being precisely analogous to that involved in the preparation of Hydrochloric Acid.

Properties.—A deliquescent salt, occurring in small and imperfect crystals. Very soluble in water; the solution acting upon glass in the same manner as Hydrofluoric Acid.

POTASSIUM, IODIDE OF.

Symbol, KI. Atomic weight, 166.

This salt is usually prepared by dissolving Iodine in Liquor Potassæ until the solution begins to acquire a brown colour: a mixture of Iodide of Potassium and *Iodate of Potash* ($KO\,IO_5$) is thus formed; but by evaporation and heating to redness, the latter salt parts with its Oxygen, and is converted into Iodide of Potassium.

Properties.—It forms cubic and prismatic crystals, which are hard, and very slightly or not at all deliquescent. Soluble in less than an equal weight of water at 60°; it is also soluble in Alcohol, but not in Ether. The proportion of Iodide of Potassium contained in a saturated alcoholic solution, varies with the strength of the spirit,—with common Spirits of Wine, sp. gr. ·836, it would be about 8 grains to the drachm; with Alcohol rectified from Carbonate of Potash, sp. gr. ·823, 4 or 5 grains; with Alcohol of ·805, 2 grains. The solution of Iodide of Potassium is instantly coloured brown by free Chlorine; also very rapidly by Nitric Acid containing Peroxide of Nitrogen; ordinary acids however act less quickly, Hydriodic Acid being first formed, and subsequently decomposing spontaneously.

Commercial Iodide of Potassium.—A very pure Iodide of Potassium has lately been prepared purposely for Photography, in crystals which have a slightly yellow tinge. Much of the Iodide, however, employed for medical and other purposes, is contaminated with foreign salts.

Carbonate of Potash is the most common impurity:

when it is present, the Iodide forms small and imperfect crystals, which become moist on exposure to the air, from the deliquescent nature of the Alkaline Carbonate.

Sulphate of Potash is also a common impurity; it may be detected by Chloride of Barium. Chloride of Potassium, when present in the Iodide, may be detected as follows:—Precipitate the salt by an equal weight of Nitrate of Silver, and treat the yellow mass with solution of Ammonia: if any Chloride of Silver be present, it dissolves in the Ammonia, and, after filtration, is precipitated in white curds by the addition of an excess of pure Nitric Acid. If the Nitric Acid employed is not pure, but contains traces of free Chlorine, the Iodide of Silver must be well washed with distilled water before treating it with Ammonia, or the excess of free Nitrate of Silver dissolving in the Ammonia would, on neutralizing, produce Chloride of Silver, and so cause an error.

Iodate of Potash is a fourth impurity often found in Iodide of Potassium: to detect it, add a drop of dilute Sulphuric Acid, or a crystal of Citric Acid, to the solution of the Iodide; if much Iodate be present, the liquid will become yellow in a few minutes from liberation of free Iodine. The *rationale* of this reaction is as follows:—The Sulphuric Acid unites with the base of the salt, and liberates Hydriodic Acid (HI), which is a colourless compound; but if Iodic Acid (IO_5) be also present, it decomposes the Hydriodic Acid first formed, oxidizing the Hydrogen into Water (HO), and setting free the Iodine. The immediate production of a yellow colour on adding a weak acid to aqueous solution of Iodide of Potassium, is therefore a proof of the presence of an Iodate.

Tests for purity of Iodide.—Solution of Chloride of Barium is commonly used to detect impurities in Iodide of Potassium; it forms a white precipitate if Carbonate, Iodate, or Sulphate be present. In the two former instances the precipitate dissolves on the addition of a single drop of *pure* dilute Nitric Acid, but in the latter case it is insoluble. The commercial Iodide however is rarely so pure as to remain quite clear on the addition of Chloride of Barium.

A simple test for Carbonate of Potash, which is the most objectionable impurity, is to dissolve the Iodide in about three times its weight of Lime water; a turbidity will indicate the presence of Carbonate.

The mere fact of reddened Litmus-paper becoming blue in solution of Iodide of Potassium is no proof of impurity, since the finest crystals which can be obtained have an alkaline reaction. But if an Alcoholic solution of the Iodide remains quite colourless when exposed for several days to a strong light, it is almost certain that an excess of alkali is present: the chemically pure Iodide of Potassium is gradually decomposed by light, and assumes a faint straw-yellow tint, returning however to its colourless condition on putting the bottle again in a dark place.

Iodide of Potassium may, when required, be purified by recrystallizing it from Spirit, or by dissolving it in Alcohol of ·805, in which Carbonate, Sulphate, and Iodate are insoluble.

POTASSIUM, SULPHIDE OF.

There are many Sulphides of Potassium, but the one commonly employed by Photographers, and sold in commerce as "Liver of Sulphur," is an impure Tersulphide. It is prepared by heating Sulphur with Carbonate of Potash, the result of which is that a portion of the Sulphur is oxidized into Sulphuric Acid, and combines with Potash, forming Sulphate of Potash, whilst another portion enters into combination with Potassium, producing a Sulphide of Potassium containing three atoms of Sulphur to one of Potassium.

Sulphide of Potassium is used for the same purposes as Hydrosulphate of Ammonia, *q. v.*

PYROGALLIC ACID.

Symbol, $C_8H_4O_4$ (Stenhouse). Atomic weight, 84.

The preparation and properties of Pyrogallic Acid have been sufficiently described at page 28. This substance is now made in very large quantities, and the desire of the purchaser to economize has acted injuriously upon its manufacture, as upon that of other Photographic Chemicals. The price at which Pyrogallic Acid is sold offers no inducement to the expenditure of much pains in its preparation, and hence some samples prove unsatisfactory. Impurities of an organic nature are occasionally found in Pyrogallic Acid, which have the effect of lessening its reducing powers, and of adding to the opacity of the deposit: hence, on applying it to the surface of the film, the blacks of the Negative become very dense and smoky, but the delicate shadows refuse to develope.

PYROXYLIC SPIRIT. *See* ALCOHOL, METHYLIC.

◆

PYROXYLINE.

Formula of Gun Cotton, $C_{36}H_{21}(NO_4)_9O_{30}$.

The following particulars as to the properties of Pyroxyline may be given in addition to those mentioned in Part I, page 102. When in the dry state it is rather harsh to the touch, and produces a crackling sensation between the fingers, like Starch. It is somewhat hygroscopic, but when carefully dried, is an excellent insulator of electricity, and becomes highly electric by friction. Strong Sulphuric Acid dissolves it in the cold without evolving any gas, and the solution is colourless unless fibres of unchanged cotton are present. Cold Nitric Acid of a certain strength also dissolves it slowly, but dilution with water throws it down again. Potash dissolves Gun Cotton with decomposition, and the solution contains Nitrate of Potash, Nitrite of Potash, Sugar, and an organic Salt of Potash: the properties of the latter are those of a reducing agent, and when mixed with Ammoniacal Nitrate of Silver it may be used for silvering mirrors; by absorption of oxygen it passes gradually into the state of Oxalate of Potash.

Hadow describes four varieties of Pyroxyline, under the names of compounds A, B, C, and D; they contain nine, eight, seven, and six atoms respectively of the Peroxide of Nitrogen. The first is the explosive Gun Cotton, insoluble in Ether and Alcohol. B and C, both of which dissolve in Alcoholized Ether, are distinguished from each other by the latter being soluble in Glacial Acetic Acid and in absolute Alcohol; whilst compound D, or Xyloidine, is recognized by its ethereal solution leaving an opaque film on evaporation.

SEL D'OR. *See* GOLD, HYPOSULPHITE OF.

SILVER.

Symbol, Ag. Atomic weight, 108.

This metal, the *Luna* or *Diana* of the Alchemists, is found native in Peru and Mexico; it occurs also in the form of Sulphide of Silver.

When pure it has a sp. gr. of 10·5, and is very malleable and ductile; melts at a bright red heat. Silver does not oxidize in the air, but when exposed to an impure atmosphere containing traces of Sulphuretted Hydrogen, it is slowly tarnished, from formation of Sulphide of Silver. It dissolves in strong Sulphuric Acid, but the best solvent for it is Nitric Acid.

The standard coin of the realm is an alloy of Silver and Copper, containing about one-eleventh of the latter metal.

To prepare pure Nitrate of Silver from it, dissolve in Nitric Acid by aid of heat, and evaporate until crystals are obtained. Then wash the crystals with a little dilute Nitric Acid, redissolve them in water, and crystallize by evaporation a second time.

The process is also occasionally conducted by boiling down the impure acid solution of the Silver to dryness, without any crystallization, and fusing the product *very strongly*, so as to decompose the Nitrate of Copper: afterwards recrystallizing as before.

SILVER, ACETATE OF.

Symbol, AgO ($C_4H_3O_3$). Atomic weight, 167.

This is a difficultly soluble salt, deposited in white lamellar crystals when an Acetate is added to a strong solution of Nitrate of Silver.

The properties of Acetate of Silver have been partly described at page 134. It is sometimes used as an addition to the Negative Nitrate Bath, but the commercial Acetate of Silver being often impure and contaminated with Carbonate of Silver,—which would make the Bath alkaline,—it is better to use the Acetate of Soda, as described at page 410.

SILVER, ALBUMINTAE OF.

This name has been given by Physiological Chemists to the insoluble white substance precipitated on adding Nitrate of Silver to a solution of Albumen, and which analysis shows to contain Oxide of Silver combined with the animal matter. It is reducible to a red subcompound, both by white light and by Hydrogen Gas.

SILVER, AMMONIO-NITRATE OF.

Crystallized Nitrate of Silver absorbs Ammoniacal gas rapidly, with production of heat sufficient to fuse the resulting compound, which is white, and consists of 100 parts of the Nitrate + 29·5 of Ammonia. The compound however which Photographers employ under the name of Ammonio-Nitrate of Silver may be viewed more simply as a solution of the Oxide of Silver in Ammonia, without reference to the Nitrate of Ammonia necessarily produced in the reaction.

Very strong Ammonia, in acting upon Oxide of Silver, converts it into a black powder, termed *Fulminating Silver*, which possesses the most dangerous explosive properties. Its composition is uncertain. In preparing Ammonio-Nitrate of Silver by the common process, the Oxide first precipitated occasionally leaves a little black powder behind, on re-solution; this does not appear however, according to the observations of the Author, to be Fulminating Silver.

In sensitizing salted paper by the Ammonio-Nitrate of Silver, *free Ammonia* is necessarily formed. Thus—

Chloride of Ammonium + Oxide of Silver in Ammonia
=Chloride of Silver + Ammonia+Water.

SILVER, BROMIDE OF.

Symbol, AgBr. Atomic weight, 188.

See Part I., page 17.

SILVER, CARBONATE OF.

Symbol, $AgO\ CO_2$. Atomic weight, 138.

This is a white or yellowish powder deposited on adding any soluble Carbonate to solution of Nitrate of Silver. It is only slightly soluble in water, or in solution of Nitrate of Silver, but yet sufficiently so to produce an alkaline reaction to Litmus. More soluble in water containing Nitrate of Ammonia, and freely so in Ammonia itself. Also dissolved by dilute Nitric or Acetic Acid, forming a Nitrate or Acetate.

SILVER, CHLORIDE OF.

Symbol, AgCl. Atomic weight, 143·5.

The preparation of properties of Chloride of Silver are given in Part I., page 14.

SILVER, CITRATE OF.

Symbol, 3 AgO, Ci.

A white salt precipitated on adding a soluble Citrate to solution of Nitrate of Silver. Its property of being reduced to a coloured subsalt by the action of light, or by a deoxidizing agent, renders it useful in Photography. It is remarkable as containing a large portion of the basic constituent, viz. 3 atoms to one of Acid.

Citric Acid added to solution of Nitrate of Silver produces no precipitation.

SILVER, FLUORIDE OF.

Symbol, AgF. Atomic weight, 127.

This compound differs essentially from those last described in being soluble in water. The dry salt fuses on being heated, and is reduced by a higher temperature, or by exposure to light.

SILVER, HYPOSULPHITE OF.

Symbol, $AgO\ S_2O_2$. Atomic weight, 164.

This salt is fully described in Part I., page 199. For the properties of the soluble double salt of Hyposulphite of Silver and Hyposulphite of Soda, see page 57.

SILVER, IODIDE OF.

Symbol, AgI. Atomic weight, 235.

See Part I., page 16.

SILVER, NITRATE OF.

Symbol, $AgO\ NO_5$. Atomic weight, 170.

Preparation and Properties.—The general theory of the preparation and properties of Nitrate of Silver have been sufficiently described in the First Part of this Work (p. 12), to which the reader is referred. There are, however, some points of practical importance yet to be considered.

Pure Nitrate of Silver may be made from the standard coin of the realm, as described in page 521, art. Silver; but since the heat which is necessary to decompose the

Nitrate of Copper often produces Nitrite of Silver, it is advised that Silver nearly free from Copper should be chosen in preference. The consumption of Nitrate of Silver in Photography has now become very large, and it fortunately happens that the crystallized salt can be obtained in almost any quantity at a moderate price, being a bye-product in the operations of parting Gold and Silver, which are carried on in the refineries. The assay processes also yield a portion of the Nitrate sold in commerce, but not by any means the greater part.

This facility of obtaining commercial crystallized Nitrate of Silver at a price which is very little above that of the metal it contains, has however acted injuriously as regards the purity of the article, since it necessarily leaves its manufacture in the hands of a few individuals, who are not able to pay that attention to it which is needed. The crystals are usually sent out simply dried off from the Nitric Acid, as a refuse product on which no profit can be expected. Intentional adulteration, however, is not practised by the large producers of Nitrate of Silver, as far as the Author is aware.

Nitrate of Potash and Nitrate of Copper have been spoken of as occasional impurities in commercial Nitrate of Silver, but the presence of these salts in small quantity would have little effect except in reducing the strength of the Baths. The peculiar Photographic action of bad Nitrate of Silver (p. 135) is probably to be referred to a different cause, viz. to the presence of oxidized organic matter. In the assay processes, fragments of charcoal are introduced to prevent the acid from *bumping* as it dissolves the Silver, and although it has been conjectured that no oxidation of the carbon takes place, yet such is not the fact. On the contrary, we have good reason for believing that in presence of Nitrate of Silver Nitric Acid oxidizes charcoal into a substance which has an affinity for the Silver salt; and the Author has found that Nitrate of Silver so produced is altogether unfit for Collodion Photography (see p. 411).

When old Nitrate Baths are precipitated by Zinc, organic matter is carried down by the reduced Silver, and the product, if converted into Nitrate of Silver without previous fusion, is useless for Photographic purposes.

The Author has also detected impurity of a similar kind, but in less quantity, in cases where no charcoal had been employed. Pieces of straw, etc., may perhaps fall into the acid; but, however this may be, the fact is certain, that Nitrate of Silver prepared by dissolving Silver in Nitric Acid, and evaporating to dryness without any crystallization, cannot be depended on for Photography.

It has been suggested that the Nitrate of Silver for the Bath should be made purposely by dissolving pure Silver in pure Nitric Acid. Probably however no manufacturer would care to compete with the refiners, who are in a better position to supply the article at a reasonable price. *Recrystallization* seems therefore to be the proper remedy. The first crop of crystals may be dried off from the acid, and then crystallized a second time from distilled water; after which the product will be in a pure state if charcoal and substances of that kind have been excluded. This second crystallization ought not, according to a competent authority, to add more than fourpence, or at most sixpence, to the price per ounce.

A saturated solution of the purified crystals slowly restores the blue colour of reddened litmus-paper, if the Nitric Acid be expelled by heating to 240° previous to the second crystallization. This proceeding, however, is not actually necessary, inasmuch as a trace of adhering Nitric Acid can always be removed by Carbonate of Soda when making the Bath; and it is well known that the presence of a little acid facilitates the crystallization of Nitrate of Silver.

SILVER, NITRITE OF.

Symbol, $AgO\ NO_3$. Atomic weight, 154.

Nitrite of Silver is a compound of Nitrous Acid, or NO_3, with Oxide of Silver. It is formed by heating Nitrate of Silver, so as to drive off a portion of its Oxygen, or more conveniently, by mixing Nitrate of Silver and Nitrate of Potash in equal parts, fusing strongly, and dissolving in a small quantity of boiling water: on cooling, the Nitrite of Silver crystallizes out, and may be purified by pressing in blotting-paper.

Properties.—Nitrite of Silver is soluble in 120 parts of cold water: easily soluble in boiling water, and crystallizes on cooling, in long slender needles. It has been used in the Negative Nitrate Bath to increase the intensity of the developed image, but its tendency to favour solarization and fogging is an objection.

Properties of Nitrous Acid.—This substance possesses very feeble acid properties, its salts being decomposed even by Acetic Acid. It is an unstable body, and splits up, in contact with water, into Binoxide of Nitrogen and Nitric Acid. The Peroxide of Nitrogen, NO_4, is also decomposed by water, and yields the same products.

SILVER, OXIDE OF.

Symbol, AgO. Atomic weight, 116.

This compound has already been described in Part I., page 17.

SILVER, SULPHIDE OF.

Symbol, AgS. Atomic weight, 124.

This compound, sometimes termed Sulphuret of Silver, is formed by the action of Sulphur upon metallic Silver, or of Sulphuretted Hydrogen or Hydrosulphate of Ammonia upon the Silver salts: the decomposition of Hyposulphite of Silver also furnishes the black Sulphide.

Sulphide of Silver is insoluble in water, and nearly so in those substances which dissolve the Chloride, Bromide, and Iodide, such as Ammonia, Hyposulphites, Cyanides, etc.; but it dissolves in Nitric Acid, being converted into soluble Sulphate and Nitrate of Silver.

The colour of precipitated Sulphide of Silver varies with the quantity present; it is black when in mass, but yellowish-brown in a state of fine division.

SODA, ACETATE OF.

Symbol, $NaO, AcO_3 + 6 Aq$.

An easily crystallizable salt, employed commercially as a source of Acetic Acid. There are several qualities, some of which contain brown empyreumatic matter, but the recrystallized salt can usually be obtained pure. It is readily soluble in water and also in Alcohol.

This Acetate is undoubtedly the best form to employ in Photography, since Acetate of Potash is deliquescent, and cannot easily be kept dry.

SODA, CARBONATE OF.

Symbol, $NaO\ CO_2 + 10 Aq$.

This salt was formerly obtained from the ashes of seaweeds, but is now more economically manufactured on a large scale from common Salt. The Chloride of Sodium is converted into Sulphate of Soda, and the Sulphate into Carbonate of Soda.

Properties.—The perfect crystals contain ten atoms of water, which are driven off by the application of heat, leaving a white power—the anhydrous Carbonate. *Common Washing Soda* is a Protocarbonate, contaminated to a certain extent with Chloride of Sodium and Sulphate of Soda. The Carbonate used for effervescing draughts is either a Bicarbonate with 1 atom of water, or a Sesquicarbonate, containing about 40 per cent. of real alkali; it is therefore nearly double as strong as the washing Carbonate, which contains about 22 per cent. of Soda. Neutral or Protocarbonate of Soda is soluble in twice its weight of water at 60°, the solution being strongly alkaline.

Bicarbonate or Sesquicarbonate of Soda is less soluble than the ordinary Carbonate, requiring from ten to thirteen parts of cold water to retain it in solution: the liquid is usually milky until it has been filtered.

SODA, CITRATE OF.

This salt, the composition of which is analogous to the Citrate of Silver, *q. v.*, yields well-defined crystals, but as it is sometimes difficult to obtain it in commerce, instructions are given in this Work for making it extemporaneously by neutralizing 56 grains of pure Citric Acid with 66 grains of dry Sesquicarbonate of Soda, quantities which will yield 100 grains of Citrate of Soda.

The crystals are very soluble in water, and produce a white flocculent deposit of Citrate of Silver in solution of Nitrate of Silver.

SODA, HYPOSULPHITE OF.

Symbol, NaO, S_2O_2+5 Aq. Atomic weight, 124.

The properties of Hyposulphurous Acid and the Hyposulphite of Soda have been described at pages 57 and 199 of the present Work. The crystallized salt includes five atoms of water of crystallization.

Hyposulphite of Soda is now made on an extensive scale, and is sold at a low price. Some of the inferior qualities have a yellow colour, and are said to contain a portion of Sulphide or free Sulphur. Repeated recrystallization has been tried, but most of the Salt sold in commerce is sufficiently pure in the state in which it comes from the manufacturers. A test recommended for purity of Hyposulphite is to ascertain how much of crystallized Iodine it will dissolve. Free Iodine converts Hyposulphite of Soda into Tetrathionate of Soda; and if the salt be pure, it ought to take up half its weight of Iodine without becoming coloured.

SODA, PHOSPHATE OF.

Formula, $2\ NaO, HO, PO_5+24\ Aq.$

There are several Phosphates of Soda, but the one sold in commerce as the "Rhombic Phosphate" is the most important and the most generally known. It forms large transparent crystals which effloresce, and become opaque on the exterior; soluble in four parts of cold water, the solution possessing a faint alkaline reaction; precipitates Nitrate of Silver yellow.

Pyro-Phosphate of Soda, so called, is prepared by heating the ordinary Phosphate, and is distinguished from it by precipitating Nitrate of Silver white instead of yellow; it crystallizes in prisms.

SODIUM, AURO-CHLORIDE OF.

Formula, $NaCl, AuCl_3+4\ Aq.$

This salt is a double Chloride of Gold and Sodium, with four atoms of water of crystallization. It has been proposed as a convenient substitute for the ordinary Chloride of Gold, being hard and non-deliquescent. Another advantage also promised, was the absence of free acid in the double salt, whereas the ordinary Chloride of Gold always contains Hydrochloric Acid. The Auro-Chloride however will not in all probability come into general use in Photography, since it is evidently open to adulteration, and although theoretically neutral, yet the manufacturers themselves allow that it will not be safe to calculate upon perfect neutrality, since traces of Hydrochloric Acid are apt to remain in the interstices of the crystals.

The mode of preparing Auro-Chloride of Sodium is to add the theoretical quantity of Chloride of Sodium to a solution of Chloride of Gold, and to evaporate to dryness: the excess of Hydrochloric Acid is then dissipated, and the two Chlorides remain in a state of combination.

SODIUM, CHLORIDE OF.

Symbol, $NaCl$. Atomic weight, 58·5.

Common Salt exists abundantly in Nature, both in the form of solid rock-salt, and dissolved in the waters of the ocean.

Properties.—Fusible without decomposition at low redness, but sublimes at higher temperatures; the melted salt concretes into a hard white mass on cooling. Nearly insoluble in absolute Alcohol, but dissolves in minute quantity in rectified spirit. Soluble in three parts of water, both hot and cold. Crystallizes in cubes, which are anhydrous.

Impurities of Common Salt.—Table Salt often contains large quantities of the Chlorides of Magnesium and Calcium, which, being deliquescent, produce a dampness by absorption of atmospheric moisture: Sulphate of Soda is also commonly present. The salt may be purified by repeated recrystallization, but it is more simple to prepare the pure compound *directly*, by neutralizing Hydrochloric Acid with Carbonate of Soda.

SUGAR OF MILK. *See* MILK.

SULPHURETTED HYDROGEN.

See HYDROSULPHURIC ACID.

SULPHURIC ACID.

Symbol, SO_3. Atomic weight, 40.

Sulphuric Acid may be formed by oxidizing Sulphur with boiling Nitric Acid; but this plan would be too expensive to be adopted on a large scale. The commercial process for the manufacture of Sulphuric Acid is exceedingly ingenious and beautiful, but it involves many complicated reactions. The Sulphur is first burnt into gaseous Sulphurous Acid (SO_2), and then, by the agency of Binoxide of Nitrogen gas, an additional atom of Oxygen is imparted from the atmosphere, so as to convert the SO_2 into SO_3, or Sulphuric Acid.

Properties.—Anhydrous Sulphuric Acid is a white crystalline solid. The strongest liquid acid always contains one atom of water, which is closely associated with it, and cannot be driven off by the application of heat.

This *mono-hydrated* Sulphuric Acid, represented by the formula $HO\,SO_3$, is a dense fluid, having a specific gravity of about 1·845; boils at 620°, and distils without decomposition. It is not volatile at common temperatures, and therefore does not *fume* in the same manner as Nitric or Hydrochloric Acid. The concentrated acid may be cooled down even to zero without solidifying; but a weaker compound, containing twice the quantity of water, and termed *glacial* Sulphuric Acid, crystallizes at 40° Fahr. Sulphuric Acid is intensely acid and caustic, but it does not destroy the skin or dissolve metals so readily as Nitric Acid. It has an energetic attraction for water, and when the two are mixed, condensation ensues, and much heat is evolved; four parts of acid and one of water produce a temperature equal to that of boiling water. Mixed with aqueous Nitric Acid, it forms the liquid known as Nitro-Sulphuric Acid.

Sulphuric Acid possesses intense chemical powers, and displaces the greater number of ordinary acids from their salts. It *chars* organic substances, by removing the elements of water, and converts Alcohol into Ether in a similar manner. The *strength* of a given sample of Sulphuric Acid may be calculated, nearly, from its specific gravity, and a Table is given by Dr. Ure for that purpose. (See Appendix.) It is quite necessary however that the temperature should be attended to in taking the specific gravity, since a few degrees higher or lower than the point mentioned cause a considerable difference.

Impurities of Commercial Sulphuric Acid.—The liquid acid sold as *Oil of Vitriol* is tolerably constant in composition, and seems to be as well adapted for Photographic use as the *pure* Sulphuric Acid, which is far more expensive. The specific gravity is often about 1·836 at 60°, but an acid of 1·843 or 1·845 at 60° Fahr. can always be obtained of the manufacturers, and is preferable for employment in Photography. If a drop, evaporated upon Platinum foil, gives a fixed residue, probably Bisulphate of Potash is present. A milkiness, on dilution, indicates Sulphate of Lead; a little Sulphate of Lead however would not interfere, and may be disregarded. Commercial Sulphuric Acid usually bleaches Sulphate of Indigo, on boiling a diluted solution: this is due to traces of Nitric Acid present in the Oil of Vitriol.

Test for Sulphuric Acid.—If the presence of Sulphuric Acid, or a soluble Sulphate, be suspected in any liquid, it may be tested for by adding a few drops of dilute solution of Chloride of Barium, or of Nitrate of Baryta. A white precipitate, *insoluble in Nitric Acid*, indicates Sulphuric Acid. If the liquid to be tested is very acid, from Nitric or Hydrochloric Acid, it must be largely diluted before testing, or a crystalline precipitate will form, caused by the sparing solubility of the Chloride of Barium itself in acid solutions.

TANNIN.

Various organic substances, possessing an astringent action, have been termed "Tannin;" such, for instance, as the extractive matters from bark, used in tanning hides, the astringent principles of Tea and Coffee, etc. The most important however is the Tannin of the Gall Nut, known as "Tannic Acid" or "Gallo-Tannic Acid."

Gall Nuts contain as much as two-thirds of their weight of Tannic Acid, which is extracted by reducing the nuts to powder, and digesting them with washed Ether: the decanted liquid separates on standing into two portions. the lower being an aqueous solution of Tannic Acid, the watery constituent of which is derived from the *washed* Ether (see "Ether"). On evaporating the aqueous solution to dryness, a porous buff-coloured residue of Amorphous Tannic Acid is obtained.

Tannic Acid is freely soluble in water, but it rarely yields a clear solution, on account of traces of remaining resinous matter. The reaction to test-paper is slightly acid, and on adding an alkali a "Tannate" is formed, but the alkaline Tannates are very unstable, and tend to absorb Oxygen and become brown. Tannic Acid gives with the Persalts of Iron a violet-black precipitate, which is the basis of common writing Ink. Solutions of Gelatine are precipitated by Tannic Acid in the form of Tanno-Gelatine, or Leather : Albumen is also coagulated by Tannin. When Tannic Acid is heated to about 600° Fahr., it is decomposed, and yields Pyrogallic Acid. Nitrate of Silver is not precipitated by Tannic Acid, but suffers a slow reduction to the state of Metallic Silver.

TETRATHIONIC ACID.

Symbol, S_4O_5. Atomic weight, 104.

This acid is one of the Oxides of Sulphur, belonging to the interesting series designated by Berzelius the "Polythionic Acids." The composition of this series may be represented as follows:—

	Sulphur.	Oxygen.	Formulæ.
Dithionic or Hyposulphuric Acid	2 atoms	5 atoms	S_2O_5
Trithionic Acid	3 "	5 "	S_3O_5
Tetrathionic Acid	4 "	5 "	S_4O_5
Pentathionic Acid	5 "	5 "	S_5O_5

The amount of *Oxygen* in all is the same, that of the other element increases progressively; hence the highest member of the series might *by losing Sulphur* descend gradually until it reached the condition of the lowest. Such a transition is not only theoretically possible, but there is an actual tendency to it, all the acids being unstable with the exception of the Hyposulphuric. The Alkaline Salts of these acids are more unstable than the acids themselves; a solution of Tetrathionate of Soda becomes milky in the course of a few days from deposition of Sulphur, and, if tested, is then found to contain *Tri*thionate and eventually *Di*thionate of Soda.

The presence of Hyposulphite of Soda increases the instability of Tetrathionate of Soda. A solution of the latter may be preserved for many hours unchanged: but if a few crystals of Hyposulphite of Soda be dropped in, it begins very shortly to deposit Sulphur, and continues to do so for several days. At the same time the liquid acquires *an acid reaction* to test-paper, and produces effervescence on the addition of Carbonate of Lime.

Tetrathionate of Soda may be formed by acting on Hyposulphite of Soda with Iodine; a colourless solution is obtained, which, in addition to the new salt, contains Iodide of Sodium. Perchloride of Iron, Chloride of Copper, and Chloride of Gold, decompose Hyposulphite of Soda and form Tetrathionate, amongst other products. Acids in a free state have often the same effect, since they liberate Sulphurous Acid, which, in contact with Hyposulphite of Soda, forms Trithionate and Tetrathionate of Soda.

URANIUM, NITRATE OF.

Symbol, $U_2O_3NO_5+6$ Aq.

This salt may be formed by dissolving either of the Oxides of Uranium in Nitric Acid and evaporating over a water bath. It forms crystals of a greenish-yellow colour, which are efflorescent in warm dry air. Soluble in water, Alcohol, and Ether.

Nitrate of Uranium is not an expensive salt, and has an advantage in that respect over the Tartrate, which has been recommended in preference. Its solution in Ether exposed to the sun's rays, deposits a green Oxide, and the protoxide remains in the solution.

WATER.

Symbol, HO. Atomic weight, 9.

Water is an Oxide of Hydrogen, containing single atoms of each of the gases.

Distilled water is water which has been vaporized and again condensed; by this means it is freed from earthy and saline impurities, which, not being volatile, are left in the body of the retort. *Pure* distilled water leaves no residue on evaporation, and should remain perfectly clear on the addition of Nitrate of Silver, *even when exposed to the light;* it should also be neutral to test-paper.

The condensed water of steam-boilers, often sold in provincial towns and elsewhere as distilled water, is apt to be contaminated with oily and empyreumatic matter, which discolours Nitrate of Silver, and is therefore injurious. Newly made metal stills also fail at first in giving a pure product, from the presence of grease or dust in the soldered joints.

Rain-water, having undergone a natural process of distillation, is free from inorganic salts, but it usually contains a minute portion of *Ammonia*, which gives it an alkaline reaction to test-paper. It is very good for Photographic purposes if collected in clean vessels, but when taken from a common rain-water tank should always be examined, and if much organic matter be present, tingeing it of a brown colour, and gradually reducing Nitrate of Silver in presence of light, it must be rejected.

Spring or *River* water, commonly known as "hard water," usually contains Sulphate of Lime, and Carbonate of Lime dissolved in Carbonic Acid; also Chloride of Sodium in greater or less quantity. On boiling the water for twenty minutes or half an hour, the Carbonic Acid gas is evolved, and the greater part of the Carbonate of Lime (if any be present) deposits, forming an incrustation, which dissolves in Acetic Acid with effervescence. Spring-water is less likely to contain brown organic matter than rain-water.

In testing water for Carbonates, Sulphates, and Chlorides, divide it into two parts, and add to the first a dilute solution of Chloride of Barium, and to the second, Nitrate of Silver,*—a milkiness indicates the presence of either

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* The *Photographic Nitrate Bath* cannot be used as a test, since the Iodide of Silver it contains is precipitated on dilution, giving a milkiness which might be mistaken for Chloride of Silver.

Carbonate or Sulphate in the first case, or of Carbonate or Chloride in the second. Next, acidify the two liquids with a few drops of Glacial Acetic Acid: if the opalescence disappears and the fluid becomes clear, Carbonates are present; but if, as is more frequently the case, the cloudiness is only partially removed by the Acetic Acid, then the Carbonate is mixed with Sulphate or Chloride as the case may be.

Water for the Nitrate Bath.—Common hard water can often be used for making a Nitrate Bath when nothing better is at hand. The Chlorides it contains are precipitated by the Nitrate of Silver, leaving small quantities of soluble *Nitrates* in solution, which are not injurious. Carbonate of Lime, if present, neutralizes acid, and renders the Bath alkaline in the same manner as Carbonate of Soda (p. 133). Sulphate of Lime causes no precipitation, and ought not theoretically to produce any injurious effect. It has however been spoken against by some, but whether from practical experience or not the Writer is uninformed. Organic matter will almost certainly be injurious to the Bath, and therefore unless the purity of the rain-water can be guaranteed, spring-water will be preferable.

Water for the developing solutions.—Carbonate of Lime in a water ought not to unfit it for the developing liquid in presence of free Acetic Acid, because the chalk would be decomposed under such circumstances, and converted into Acetate of Lime, which would probably assist a little in increasing the intensity. In the case of Sulphate of Iron, chalky water throws down a small quantity of the green Protocarbonate of Iron, which produces turbidity and a rusty colour at the edges; but any acid added to the developer dissolves it and renders the liquid again clear. Chalk in water used for the Gallic Acid developer, makes it discolour quickly with Nitrate of Silver, but a minim of Acetic Acid to each two ounces is a remedy, as before shown.

Soluble Chlorides are always injurious in water used for developing, because they decompose the Nitrate of Silver on the film, producing a curdy precipitate and lessening the available strength. Acids have no effect in removing Chlorides, but they may be separated by shaking up the water with a graduated quantity of Nitrate of Silver, and filtering it. In this process however there is always a difficulty in knowing how much of the Nitrate will be needed, since the least excess over the quantity required to decompose the salt, causes the water to blacken on adding Pyrogallic Acid. This might be obviated however by keeping the Pyrogallic Acid dissolved in Glacial Acetic Acid, and adding the water only when required. Bear in mind also that it will not be necessary to remove every trace of salt from the water, since it is quite possible to bring out a perfect image with a developing solution which produces a decided turbidity on first touching the film; especially so if a few drops of solution of Nitrate of Silver be added to the developer immediately before use.

Water for washing preserved plates.—A faint opalescence on adding a few drops of solution of Nitrate of Silver may be disregarded, but if the water becomes decidedly milky, try the following mode of purifying it. To each pint add a fluid drachm of the Negative Nitrate Bath, and set it aside for twelve hours to deposit. It may be filtered at the time, but the precipitate is liable to choke the filter and make it run slowly. The above proceeding will probably leave one of the two precipitating salts in excess, but the Writer gives the proportions which he found to answer in the case of a hard water drawn from a well at the seaside, containing a mixture of Chloride of Sodium and Carbonate of Lime. Graduated quantities of the Nitrate Bath were dropped into this water at intervals of a few hours, and it was found that all further precipitation ceased when 60 minims had been added to each pint.

APPENDIX.

QUANTITATIVE TESTING OF SOLUTIONS OF NITRATE OF SILVER.

THE amount of Nitrate of Silver contained in solutions of that salt may be estimated with sufficient delicacy for ordinary Photographic operations by the following simple process.

Take the *pure* crystallized Chloride of Sodium,—which operative chemists make purposely for analysis by dissolving the best Carbonate of Soda in pure Hydrochloric Acid,—and either dry it strongly or fuse it at a moderate heat, in order to drive off any water which may be retained between the interstices of the crystals; then dissolve in distilled water, in the proportion of 8½ grains to 6 fluid ounces.

In this way, a standard solution of salt is formed, each drachm of which (containing slightly more than one-sixth of a grain of salt) will precipitate half a grain of Nitrate of Silver.

To use it, measure out accurately one drachm of the Bath in a minim measure and place it in a two-ounce stoppered phial, taking care to rinse out the measure with a drachm of distilled water, and to add the rinsings to the fluid drachm of bath; then pour in the salt solution, in the proportion of a drachm for every 4 grains of Nitrate *known to be present* in an ounce of the Bath which is to be tested; shake the contents of the bottle briskly, until the white curds have perfectly separated, and the supernatant liquid is clear and colourless; then add fresh portions of the standard solution of salt by 30 minims at a time, with constant shaking. When the last addition causes no *milkiness*, read off the total number of drachms employed (the last half-drachm being subtracted), and multiply that number by 4 for the weight in grains of the Nitrate of Silver present in an ounce of the Bath.

In this manner the strength of the Bath will be indicated within two grains to the ounce, or even to a single grain if the last additions of standard salt-solution be made in portions of 15, instead of 30 minims.

Supposing the Bath to be tested is thought to contain about 28 grains of Nitrate to the ounce, it will be convenient to begin by adding to the measured drachm, 6 *drachms* of the standard solution; afterwards, as the milkiness and precipitation become less marked, the process must be carried on more cautiously, and the bottle shaken violently for several minutes, in order to obtain a clear solution. A few drops of Nitric Acid added to the Nitrate of Silver facilitate the deposition of the Chloride; but care must be taken that the sample of Nitric Acid employed is pure and free from Chlorine, the presence of which would cause an error.

The Photographer may perhaps require to perform the operation now described when pure Chloride of Sodium is not immediately obtainable. In that case the ordinary commercial Chloride of Ammonium may be substituted, 7¾ grains being dissolved in 6 fluid ounces of water. It is advisable however, when using a Chloride of doubtful purity, to take the precaution of trying the strength of the standard saline solution, by testing it upon 30 grains of pure dried Nitrate of Silver dissolved in an ounce of water.

The above process, although sufficient for common purposes, is not likely to give exact results in the hands of the amateur. Ordinary fluid measures are seldom graduated with perfect accuracy, and hence the "burette" which the opticians construct purposely for bath testing is preferable: by its employment the necessity for calculations will be avoided, since the number of measures are made to indicate grains per ounce.

RECOVERY OF SILVER AND GOLD FROM WASTE SOLUTIONS AND RESIDUES.

a. *Separation of metallic Silver from old Nitrate Baths.*—The Silver contained in solutions of the Nitrate, Acetate, etc. may easily be precipitated by suspending a strip of sheet Copper in the liquid; the action is complete in two or three days, the whole of the Nitric Acid and Oxygen passing to the Copper, and forming a blue solution of the Nitrate of Copper. The metallic Silver however, separated in this manner, always contains a portion of Copper, and gives a blue solution when dissolved in Nitric Acid.

The Writer has tried, on a large scale, the process of separating Silver from old Baths by suspending bars of metallic Zinc in the liquid, but the operation was not so successful as could be desired. A large tree of metallic Silver formed, and when the vessel was tapped, fell to the bottom, carrying down with it detached portions of Zinc or Oxide of Zinc. In addition to this a white precipitate was noticed towards the end of the process, and the result was, that in spite of very careful washing with warm dilute Sulphuric Acid, a sufficient quantity of Zinc remained to form a bulky slag, and prevent the Silver from running into a clear liquid in the crucible.

A better process is to commence by precipitating the Silver entirely in the form of *Chloride of Silver,* by adding common Salt until no further milkiness can be produced, and then acidifying with Hydrochloric or Nitric Acid. If the liquid be well stirred, the Chloride of Silver will sink to the bottom, and may be washed by repeatedly filling the vessel with common water, and pouring off the upper clear portion when the clots have again settled. The Chloride of Silver thus formed may afterwards be dried and reduced to metallic Silver by a process presently to be described.

b. *Washings from Positive Prints.*—In a Photographic laboratory a place should be provided for large wide-mouthed two-gallon bottles, into which washings of dishes, prints, etc., should be thrown, when they contain nothing but free Nitrate of Silver. A lump of salt will serve to keep the liquid free from Silver, and a few drops of common Muriatic Acid will acidify it, and encourage the deposition of the Chloride of Silver. The upper part of the liquid may be poured off from time to time, and when the deposit of Chloride is sufficiently thick to make it worth collecting, it may be drained on a cloth, and treated as presently to be described.

c. *Cuttings of sensitive paper.*—These should all be thrown into a waste basket and eventually burnt with free access of air: the ash will probably contain from 50 to 70 per cent. of metallic Silver, and may be treated as described at page 545 under the head of reduction of Sulphide of Silver. Cuttings of prints previously toned and fixed contain so little Silver as scarcely to repay the trouble of collecting.

d. *Waste Developing Solution.*—Amateurs would scarcely find it worth their while to economize these liquids; but for the professional Photographer who uses larger quantities, and works on plates which require much pushing of the development with Nitrate of Silver, it will be advantageous to fit up a gutta-percha sink, and to conduct away all the waste products, both developing and hypo-fixing, into one vessel. Afterwards proceed as advised below.

e. *Hyposulphite Baths.*—The Silver cannot be separated from Hypo-Baths in the same manner as from solution of the Nitrate, since both Chloride and Iodide of Silver are soluble in Hyposulphite of Soda.

In former editions the employment of Sulphuretted Hydrogen was advised; but this plan is very slow and tedious, and requires a long time to carry out. Another method is to decompose the whole of the Hyposulphite by means of the waste Nitrosulphuric Acid employed in making Pyroxyline, and so to throw down a mixture of Sulphide of Silver and free Sulphur, leaving Sulphate and Nitrate of Soda in solution. A third process, which has superseded both of these modes, is to warm the solution with a bar of suspended Zinc. After two or three hours' boiling, a portion of the liquid is filtered, after which it is examined for Silver by Sulphuretted Hydrogen. If there be no precipitation, or simply a *white* turbidity, the whole of the noble metals have been thrown down by the Zinc. Collect the precipitate therefore upon a cloth, wash it with water until a drop evaporated on platinum foil leaves no residue, dry by artificial heat, and run it down into a button with a mixture of Borax and dry Carbonate of Soda as advised in works on Analytical Chemistry. Hydrosulphate of Ammonia cannot be used instead of Sulphuretted Hydrogen to determine when the warm solution of Hyposulphite is freed from Silver, because it precipitates the white Sulphide of Zinc, and as a trace of Iron is almost invariably present, a brown colour is imparted to the deposit, which would then be mistaken for Sulphide of Silver. Collect the deposited Silver and redissolve it in Nitric Acid, afterwards throwing it down again as Chloride; this will free it from impurities, which, if present in any quantity, prevent the Silver from running in the crucible, and occasion much loss in the form of slag. The residuary part not taken up by the Nitric Acid would contain any Gold which might be present, and must be dealt with as advised in page 494.

Many practical photographers, objecting to the trouble involved in boiling with Metallic Zinc, precipitate the Silver from their Hypo-fixing baths by means of the Sulphide of Potassium, which the operative chemists now sell in lumps for that purpose. Dissolve a drachm of the Sulphide in an ounce of water, and add it until a fresh portion causes no further precipitate: it ought to decompose at least twice its weight of Nitrate of Silver, but no certain directions can be given; an excess however should be avoided if possible, since Sulphide of Gold is soluble in excess of Sulphide of Potassium, and hence, if the Silver contained Gold, it would not be thrown down under such circumstances. For the mode of dealing with the Sulphide of Silver, see page 545.

f. *Alkaline Chloride of Gold toning Solution.*—Throw the exhausted toning Bath into a large bottle, and when a sufficiency has been collected, add a solution of Sulphate of Iron in the proportion of two grains of the Sulphate for each grain of Chloride of Gold originally present in the Bath. A black precipitate will fall, consisting of Carbonate and Oxide of Iron, mixed with metallic Gold: it may be dried and sent to the assayer, or may be purified as follows: Digest twenty grains in a flask with a fluid drachm of Hydrochloric Acid, fifteen minims of Nitric Acid, and two drachms of Water. After the lapse of a quarter of an hour, boil the mixture, add two ounces more of Water, and filter out the insoluble residue, which will consist principally of Chloride of Silver and organic matter. One hundred grains of Protosulphate of Iron will then throw down the whole of the Gold in a pure state. To convert the metallic Gold into Chloride of Gold, see the Vocabulary, page 494.

g. *Solution of Cyanide of Potassium.*—The liquid may be diluted largely with water, and Sulphide of Potassium added as above described, until no further precipitation of black Sulphide ensues. Collect the deposit, and treat it as advised at page 545.

h. *Reduction of Chloride of Silver to the metallic state.*—The Chloride of Silver is first to be washed, by filling up the vessel which contains it, two or three times with water, and then pouring off the liquid, or drawing it off close with a siphon. It may next be dried at a gentle heat, and fused with twice its weight of dry Carbonate of Potash, or, better still, with a mixture of the Carbonates of Potash and Soda, which is more fusible than either of the separate salts. A Cornish crucible may be used to contain the mixture, and the heat may be raised to bright redness, after which, on allowing the crucible to cool, and breaking it, a button of Silver will be found at the bottom.

The process for reducing Chloride of Silver in the moist way, by metallic Zinc and Sulphuric Acid, is conducted as follows:— The Chloride, after having been well washed as before, is placed in a large flat dish, and a bar of metallic Zinc is laid in contact with it. A small quantity of Oil of Vitriol, diluted with four parts of water, is then added, until a slight effervescence of Hydrogen gas begins to take place. The vessel is set aside for two or three days, and is not to be disturbed, either by stirring or moving the bar. The reduction begins with the Chloride immediately in contact with the Zinc, and radiates in all directions. When the whole mass has become of a grey colour, the bar is to be carefully removed and the adhering Silver washed off with a stream of water; the Zinc usually presents a honeycombed appearance, with irregularities upon the surface, which however are not metallic Silver;—they consist of Oxide of Zinc, or of some of the impurities present in commercial Zinc, such as Sulphate of Lead, Oxide of Iron, Tin, Carbon, etc.

In order to ensure the purity of the Silver, a fresh addition of dilute Sulphuric Acid must be made, after the Zinc bar has been removed, and the digestion continued for several hours, in order to dissolve any fragments of metallic Zinc which may have been inadvertently detached. The grey powder must be repeatedly washed, first with Sulphuric Acid and water (this is necessary to dissolve a portion of an insoluble Salt of Zinc, probably an oxychloride), and then with water alone, until the liquid runs away *neutral*, and gives no precipitate with Carbonate of Soda; it may then be fused into a button, to burn off organic matter if present, and subsequently converted into Nitrate of Silver by boiling with Nitric Acid diluted with two parts of water.

In reducing Chloride of Silver precipitated from old Nitrate Baths *containing Iodide of Silver*, the grey metallic powder is contaminated with unreduced Iodide of Silver, which prevents a part of the metal from readily fusing in the crucible, and so increases the amount of slag. Be careful therefore to save all the scoriæ, and to run them down separately with a mixture of Borax and Carbonate of Soda: the quantity of Silver recovered by so doing is sometimes considerable.

In some of the earlier editions of this work the importance of *fusing* the Metallic Silver before reconverting it into Nitrate was not alluded to. This omission the Writer now supplies, having found that the Chloride both before and after its reduction may retain traces of organic matter.

i. *Conversion of Sulphide into Metallic Silver.*—The black Sulphide of Silver may easily be converted into Metallic Silver, as follows:—dry and subsequently pulverize it, after which it is to be rubbed up in a mortar with about twice its weight of common Nitre. Then place a clay crucible upon the fire, and when the bottom part is heated nearly to redness, throw in the black mixture a little at a time, when immediate deflagration will ensue, and the Sulphur will be burnt away, leaving the Silver in the form of a network of metal. This Silver is sufficiently pure for dissolving in Nitric Acid if it be first cleansed by boiling in water acidified with Hydrochloric Acid, but when the requisite appliances are at hand, it will be better to run it into a button with Borax and Carbonate of Soda.

The ashes from burnt sensitive paper may be treated in a similar way, and any Chloride of Silver present in them will be reduced by the Carbon remaining unburnt.

k. *Separation of Metallic Gold from Silver.*—The deposit produced from Hyposulphite fixing and toning Baths by long boiling with Zinc, or by Sulphide of Potassium, may contain a portion of Gold as well as Silver. To separate these metals when the latter is in excess, dissolve the button in dilute Nitric Acid, and collect the small portion of insoluble matter which subsides. Wash this precipitate with dilute Ammonia, to remove Chloride of Silver, if present, and reconvert it into Chloride of Gold by the mode described in the Vocabulary, Art. "Gold, Chloride of."

PURIFICATION OF OLD COLLODION NITRATE BATHS FOR EMPLOYMENT IN PRINTING.

This operation is required in order to separate the dissolved Iodide of Silver, which if allowed to remain interferes with the rapidity of the toning action of the Gold-solutions (p. 197).

Make a solution of Citric Acid, sixteen grains in an ounce of water, and drop it into the Bath in the proportion of a fluid drachm for each eight ounces of the solution of Nitrate of Silver. This addition may or may not cause a white precipitate, but the subsequent steps are the same in either case. Next immerse a strip of blue litmus-paper, which will immediately be reddened; then add Liquor Ammoniæ drop by drop, until, after vigorous stirring, the blue colour of the reddened paper appears permanently restored. Now throw the whole on a paper filter, and when the liquid has run through, drop in an excess of pure Nitric Acid sufficient to redden the test-paper decidedly. Lastly, ascertain the strength of the liquid, and make it up to sixty grains to the ounce of water, by adding the proper quantity of crystallized Nitrate of Silver.

No exact directions can be given as to the quantities of Ammonia and Nitric Acid; but with the strongest Liquor Ammoniæ obtainable about two drops will be required for each drachm of the Citric Acid Solution. The number of drops of Nitric Acid must be varied according to the amount of the excess of Ammonia.

The *rationale* of the process is as follows:—The Citric Acid, either with or without the aid of the Ammonia, precipitates white Citrate of Silver in the Bath, and this insoluble substance carries down the Iodide of Silver with it in virtue of an affinity. Excess of Citric Acid must not be permitted to remain in the Bath, since it would cause redness in the prints. Excess of Ammonia, on the other hand, would favour discoloration of the Bath by use, and would lessen the keeping qualities of the paper in hot weather; hence a trace of Nitric Acid will be required to neutralize the alkali.*

MODE OF TAKING THE SPECIFIC GRAVITY OF LIQUIDS.

Instruments are sold, termed "Hydrometers," which indicate specific gravity by the extent to which a glass bulb containing air, and properly balanced, rises or sinks in the liquid; but a more exact process is by the use of the specific-gravity bottle.

These bottles are made to contain exactly 1000 grains of distilled water, and with each is sold *a brass weight*, which counterbalances it when filled with pure water.

In taking the specific gravity of a liquid, fill the bottle quite full and insert the stopper, which being pierced through by a fine capillary tube allows the excess to escape. Then, having wiped the bottle quite dry, place it in the scale-pan, and ascertain the number of grains required to produce equilibrium; this number added to, or subtracted from, *unity* (the assumed specific gravity of water), will give the density of the liquid.

Thus, supposing the bottle filled with *rectified Ether* to require 250 grains to enable it to counterbalance the brass weight,—then

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* Photographic Journal, vol. v. p. 138.—*F. G. Eliot.*

1· *minus* ·250, or ·750, is the specific gravity; but in the case of *Oil of Vitriol* the bottle, when full, will be *heavier* than the counterpoise by perhaps 836 grains; therefore 1· *plus* ·836, *id est* 1·836, is the density of the sample examined.

Sometimes the bottle is made to hold only 500 grains of distilled water in place of 1000: in this case the number of grains to be added or subtracted must be multiplied by 2.

In taking specific gravities, observe that the temperature be within a few degrees of 60° Fahrenheit (if higher or lower, immerse the bottle in warm or cold water); and wash out the bottle thoroughly with water each time after use.

ON FILTRATION AND WASHING PRECIPITATES.

In preparing filters, cut the paper into squares of a sufficient size, and fold each square neatly upon itself, first into a half-square, and then again, at right angles, into a quarter-square;—round off the corners with a pair of scissors, and open out the filter into a conical form, when it will be found to drop exactly into the funnel, and to be uniformly supported throughout.

Before pouring in the liquid, always moisten the filter with distilled water, in order to expand the fibres; if this precaution be neglected, the pores are apt to become choked in filtering liquids which contain finely divided matter in suspension. The solution to be filtered may be poured gently down a glass rod, held in the left hand, and directed against the side of the funnel, near to the upper part. If it does not immediately run clear, it will usually do so on returning it into the filter and allowing it to pass through a second time. When glass stirring rods are not at hand, substitute slate pencils, which are without action upon the solutions employed by photographers.

Mode of Washing Precipitates.—Collect the precipitate upon a filter and drain off as much of the mother-liquor as possible; then pour in distilled water by small portions at a time, allowing each to percolate through the deposit before adding a fresh quantity. When the water passes through perfectly pure, the washing is complete; in testing it, a single drop may be laid upon a strip of glass and allowed to evaporate spontaneously in a warm place, or the proper chemical reagents may be applied, and the washing continued until no impurity can be detected. Thus, for example, in washing the Sulphide of Silver precipitated from a solution of

Hyposulphite of Soda by means of Sulphide of Potassium, the process will be completed when the water which runs through causes no discoloration with a drop of Nitrate of Silver solution.

ON THE USE OF TEST-PAPERS.

The nature of the colouring matter which is employed in the preparation of litmus-paper has already been described at page 505.

In testing for the alkalies and basic oxides generally, the blue litmus-paper which has been reddened by an acid may be used, or, in place of it, the *turmeric* paper. Turmeric is a yellow vegetable substance which possesses the property of becoming brown when treated with an alkali; it is however less sensitive than the reddened litmus, and is scarcely affected by the weaker bases, such as Oxide of Silver.

In using test-papers, observe the following precautions:—They should be kept in a dark place, and protected from the action of the air, or they soon become purple from Carbonic Acid, always present in the atmosphere in small quantity. By immersion in water containing about one drop of Liquor Potassæ, or a grain of Carbonate of Soda to four ounces, the blue colour is restored. As the quantities which are tested for in Photography are often infinitesimally small, it is essential that the litmus-paper should be in good condition; and test-papers prepared with *porous* paper will be found to show the colour more decidedly than those upon glazed or strongly-sized paper. The mode of employing the paper is as follows:—Place a small strip in the liquid to be examined: if it becomes at once *bright red*, a strong acid is present; but if it changes *slowly* to a *wine-red* tint, a weak acid, such as Acetic or Carbonic, is indicated. In the case of the Photographic Nitrate Bath faintly acidified with Acetic Acid, a purple colour only may be expected, and a decided red colour would suggest the presence of Nitric Acid. In the Hypo fixing Bath which has acquired acidity, the litmus-paper will perhaps redden slightly in about three or four minutes.

Blue litmus-papers may be changed to the red papers used for alkalies by soaking in water acidified with Sulphuric Acid, one drop to half a pint; or by holding for an instant near the mouth of a bottle containing Glacial Acetic Acid. In examining a Nitrate Bath for alkalinity by means of the reddened litmus-paper, at least five or ten minutes should be allowed for the action, since the change of colour from red to blue takes place very slowly (p. 133): and if test-papers are left floating in any liquid whilst acids or alkalies are being added for the purpose of neutralizing, be careful not to drop the neutralizing solution *upon the paper.*

REMOVAL OF SILVER STAINS FROM THE HANDS, LINEN, ETC.

The black stains upon the hands caused by Nitrate of Silver, may readily be removed by rubbing them with a moistened lump of Cyanide of Potassium, and afterwards with a piece of pumice stone. As Cyanide of Potassium however is highly poisonous, many prefer the following plan:—Wet the spot with a saturated solution of Iodide of Potassium, and afterwards with Nitric Acid (the strong Nitric Acid acts upon the skin and turns it yellow, it must therefore be diluted with two parts of water before use); then wash with solution of Hyposulphite of Soda.

Stains upon white linen may be easily removed by brushing them with a solution of Iodine in Iodide of Potassium, and afterwards washing with water and soaking in Hyposulphite of Soda, or Cyanide of Potassium, until the yellow Iodide of Silver dissolves out; the Bichloride of Mercury (neutral solution) also answers well in many cases, changing the dark spot to white (p. 151).

The following liquid, said to contain Cyanide of Iodine, has been recommended as an energetic remover of Silver stains:—Cyanide of Potassium 100 grains; Iodine 10 grains; Water 1 ounce: the solution should be colourless.

REMOVAL OF STOPPERS AND CLEANSING OF BOTTLES.

Substances which exert a solvent action on Silica are likely to fix the stoppers of bottles; such, for instance, as Caustic Potash and Carbonate of Potash; also Iodizing solutions containing Iodide of Potassium, etc. To remove the stopper, begin by inverting the bottle for about half an hour, that the liquid may gravitate into the neck, then tap it gently, when it will probably be found to yield: if not, continue the tapping with the wooden handle of a spatula, on each side successively, so as to keep up a constant vibration. Next fix a string to the table, and having twisted it round the neck, move the bottle rapidly backwards and forwards, until a considerable amount of heat has been generated, after which the gentle tapping may be resumed. Lastly, heat the neck with a spirit lamp applied gradually and with constant movement, and when sufficient expansion has been produced, tap as before, or tie a cloth round the stopper, and twist it out by aid of a key.

In cleansing dirty bottles, consider first the nature of the impurity to be removed. If it be soluble in water, a careful rinsing two or three times repeated will be sufficient, but in other cases the proper solvent must be used, or mechanical friction resorted to. Greasy bottles are always troublesome, and are likely to soil both the bottle-brushes and the washing water. Liquor Potassæ is the best solvent, but a warm solution of common washing Soda may be substituted. Red stains of Peroxide of Iron are removed by a few drops of Hydrochloric Acid; crusts of Carbonate of Lime by the same. Brown stains of Sulphide of Silver dissolve in Nitric Acid. Varnish bottles are often most effectually cleansed by Spirit of Wine, followed by shot and water; Collodion bottles, by shot assisted by a pointed wire, to scrape away the precipitated Pyroxyline.

In using shot for cleaning, avoid those bottles which contain grease or resinous matter likely to adhere to the shot: bottle-brushes would also be soiled by using them for cleaning away any organic substance insoluble in water. When a considerable number of bottles require cleansing, begin by marking each of the stoppers, or by tying them securely to the necks, in order to avoid confusion.

REMOVAL OF VARNISH FROM GLASS PLATES.

The black varnish may often be removed from Collodion positives, by means of Chloroform or Benzole, neither of which dissolves the Pyroxyline constituting the film.

Glass plates varnished with Negative varnish, may sometimes be cleaned with Chloroform or Benzole; but when the preservation of the picture is not an object, the plates may be left soaking in a solution of washing "Soda" for several hours, after which the film will be removable by friction. A few drachms of waste Nitro-Sulphuric Acid poured over the plate, will oxidize the varnish and loosen the film in the course of half an hour.

PROTECTION OF GUTTA-PERCHA TROUGHS.

Many operators cleanse new Gutta-percha baths by washing them out with strong solution of Cyanide of Potassium, followed by dilute Nitric Acid and Water. The Writer's plan is to fill the trough with an old solution of Nitrate of Silver, useless for Photography, and after a digestion of several days to wash it with water and a bottle-brush.

Impure Gutta-percha troughs are said to be protected, as far as Nitrate of Silver is concerned, by pouring in shellac varnish, and inverting the trough until it is dry, after which a second coating may be applied. Of this method the Author knows nothing by experience, having always preferred the use of a purer form of Gutta-percha, not requiring such treatment.

VARNISH FOR BLACKING BRASS-WORK.

Take the ordinary spirit-lacquer of the shops, and rub it up with Lampblack into a thin cream, afterwards filtering through muslin. The brass-work must be heated before the black is applied, or it will give a shining instead of a lustreless surface.

A TABLE SHOWING THE QUANTITY OF ANHYDROUS ACID IN DILUTE SULPHURIC ACID OF DIFFERENT SPECIFIC GRAVITIES. (URE.)

Specific Gravity.	Real Acid in 100 parts of the Liquid.	Specific Gravity.	Real Acid in 100 parts of the Liquid.	Specific Gravity.	Real Acid in 100 parts of the Liquid.
1·8485	81·54	1·8115	73·39	1·7120	65·23
1·8475	80·72	1·8043	72·57	1·6993	64·42
1·8460	79·90	1·7962	71·75	1·6870	63·60
1·8439	79·09	1·7870	70·94	1·6750	62·78
1·8410	78·28	1·7774	70·12	1·6630	61·97
1·8376	77·46	1·7673	69·31	1·6520	61·15
1·8336	76·65	1·7570	68·49	1·6415	60·34
1·8290	75·83	1·7465	67·68	1·6321	59·52
1·8233	75·02	1·7360	66·86	1·6204	58·71
1·8179	74·20	1·7245	66·05	1·6090	57·89

A TABLE SHOWING THE QUANTITY OF ANHYDROUS ACID IN THE LIQUID NITRIC ACID OF DIFFERENT SPECIFIC GRAVITIES. (URE.)

Specific Gravity.	Real Acid in 100 parts of the Liquid.	Specific Gravity.	Real Acid in 100 parts of the Liquid.	Specific Gravity.	Real Acid in 100 parts of the Liquid.
1·5000	79·700	1·4640	69·339	1·4147	58·978
1·4980	78·903	1·4600	68·542	1·4107	58·181
1·4960	78·106	1·4570	67·745	1·4065	57·384
1·4940	77·309	1·4530	66·948	1·4023	56·587
1·4910	76·512	1·4500	66·155	1·3978	55·790
1·4880	75·715	1·4460	65·354	1·3945	54·993
1·4850	74·918	1·4424	64·557	1·3882	54·196
1·4820	74·121	1·4385	63·760	1·3833	53·399
1·4790	73·324	1·4346	62·963	1·3783	52·602
1·4760	72·527	1·4306	62·166	1·3732	51·805
1·4730	71·730	1·4269	61·369	1·3681	51·068
1·4700	70·933	1·4228	60·572	1·3630	50·211
1·4670	70·136	1·4189	59·775	1·3579	49·414

THE PROPORTION OF ABSOLUTE ALCOHOL BY WEIGHT IN 100 PARTS OF SPIRIT, OF DIFFERENT SPECIFIC GRAVITIES, AT 60° FAHR.

Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.	Alcohol per cent.	Specific Gravity.
48	·9228	69	·8745	85	·8357
50	·9184	70	·8721	86	·8331
52	·9135	71	·8696	87	·8305
54	·9090	72	·8672	88	·8279
56	·9047	73	·8649	89	·8254
58	·9001	74	·8625	90	·8228
59	·8979	75	·8603	91	·8199
60	·8956	76	·8581	92	·8172
61	·8932	77	·8557	93	·8145
62	·8908	78	·8533	94	·8118
63	·8886	79	·8508	95	·8089
64	·8863	80	·8483	96	·8061
65	·8840	81	·8459	97	·8031
66	·8816	82	·8434	98	·8001
67	·8793	83	·8408	99	·7969
68	·8769	84	·8382	100	·7938

BAUMÉ'S HYDROMETER SCALE.

A portion of the above Scale is given with a view of facilitating the translation of foreign papers, in which degrees of Baumé are often put instead of specific gravities.

For Liquids heavier than Water.

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
29	1·235	43	1·395	57	1·600
30	1·245	44	1·407	58	1·617
31	1·256	45	1·420	59	1·634
32	1·267	46	1·434	60	1·652
33	1·277	47	1·448	61	1·670
34	1·288	48	1·462	62	1·689
35	1·299	49	1·476	63	1·708
36	1·310	50	1·490	64	1·727
37	1·321	51	1·495	65	1·747
38	1·333	52	1·520	66	1·767
39	1·345	53	1·535	67	1·788
40	1·357	54	1·551	68	1·809
41	1·369	55	1·567	69	1·831
42	1·381	56	1·583	70	1·854

For Liquids lighter than Water.

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
13	0·980	29	0·885	45	0·807
14	0·973	30	0·880	46	0·802
15	0·967	31	0·874	47	0·798
16	0·960	32	0·869	48	0·794
17	0·954	33	0·864	49	0·789
18	0·948	34	0·859	50	0·785
19	0·942	35	0·854	51	0·781
20	0·936	36	0·849	52	0·777
21	0·930	37	0·844	53	0·773
22	0·924	38	0·839	54	0·768
23	0·918	39	0·834	55	0·764
24	0·913	40	0·830	56	0·760
25	0·907	41	0·825	57	0·757
26	0·901	42	0·820	58	0·753
27	0·896	43	0·816	59	0·749
28	0·890	44	0.811	60	0·745

DEGREES CENTIGRADE, COMPARED WITH THE SCALE OF FAHRENHEIT.

The Thermometric Scale in common use in France is the Centigrade. The following Table will serve for its conversion into degrees of Fahrenheit, from the freezing to the boiling point of water.

°Cent.	°Fahr.	°Cent.	°Fahr.	°Cent.	°Fahr.	°Cent.	Fahr.
0	32·0	26	78·8	51	123·8	76	168·8
1	33·8	27	80·6	52	125·6	77	170·6
2	35·6	28	82·4	53	127·4	78	172·4
3	37·4	29	84·2	54	129·2	79	174·2
4	39·2	30	86·0	55	131·0	80	176·0
5	41·0	31	87·8	56	132·8	81	177·8
6	42·8	32	89·6	57	134·6	82	179·6
7	44·6	33	91·4	58	136·4	83	181·4
8	46·4	34	93·2	59	138·2	84	183·2
9	48·2	35	95·0	60	140·0	85	185·0
10	50·0	36	96·8	61	141·8	86	186·8
11	51·8	37	98·6	62	143·6	87	188·6
12	53·6	38	100·4	63	145·4	88	190·4
13	55·4	39	102·2	64	147·2	89	192·2
14	57·2	40	104·0	65	149·0	90	194·0
15	59·0	41	105·8	66	150·8	91	195·8
16	60·8	42	107·6	67	152·6	92	197·6
17	62·6	43	109·4	68	154·4	93	199·4
18	64·4	44	111·2	69	156·2	94	201·2
19	66·2	45	113·0	70	158·0	95	203·0
20	68·0	46	114·8	71	159·8	96	204·8
21	69·8	47	116·6	72	161·6	97	206·6
22	71·6	48	118·4	73	163·4	98	208·4
23	73·4	49	120·2	74	165·2	99	210·2
24	75·2	50	122·0	75	167·0	100	212·0
25	77·0						

[Réaumur's Scale is occasionally employed in Germany, Russia, etc.: in this the freezing point of water is termed 0°, and the boiling point 80°. Each degree of Fahrenheit's scale is equal to four-ninths of a degree on Réaumur's: if therefore the number of degrees of Réaumur be multiplied by 9 and divided by 4, the quotient *plus* 32 will be the corresponding degree of Fahrenheit. Thus 80° (Réaumur) $\times 9 = 720 \div 4 = 180 + 32 = 212^\circ$ (Fahrenheit).

WEIGHTS AND MEASURES.

Troy or Apothecaries' Weight.

1 Pound = 12 Ounces. 1 Ounce = 8 Drachms. 1 Drachm = 3 Scruples. 1 Scruple = 20 Grains. (1 Ounce Troy = 480 Grains, or = 1 Ounce Avoirdupois *plus* 42·5 grains.)

Avoirdupois Weight.

1 Pound = 16 Ounces. 1 Ounce = 16 Drachms. 1 Drachm = 27·343 grains. (1 Ounce Avoirdupois = 437·5 grains.) (1 Pound Avoirdupois = 7000 Grains, or = 1 Pound Troy *plus* 2½ Troy Ounces *plus* 40 grains.)

Imperial Measure.

1 Gallon = 8 Pints. 1 Pint = 20 Ounces. 1 Ounce = 8 Drachms. 1 Drachm = 60 Minims. (A Wine Pint of water measures 16 Ounces, and weighs a Pound.)

An Imperial Gallon of water *weighs* 10 Pounds Avoirdupois, or 70,000 Grains. An Imperial Pint of water *weighs* 1¼ Pound Avoirdupois. A fluid Ounce of water *weighs* 1 Ounce Avoirdupois, or 437·5 Grains. A Drachm of water *weighs* 54·7 Grains.

French Measures of Weight.

1 Kilogramme = 1000 Grammes = something less than 2¼ Pounds Avoirdupois.

1 Gramme = 10 Décigrammes = 100 Centigrammes = 1000 Milligrammes = 15·433 English Grains.

A Gramme of water *measures* 1 Cubic Centimètre, or 17 English Minims, nearly. 1000 Grammes of water *measure* 35½ English fluid Ounces.

French Measures of Volume.

1 Litre = 10 Décilitres = 100 Centilitres = 1000 Millilitres = 35¼ English fluid Ounces.

1 Litre = Cubic Décimètre = 1000 Cubic Centimètres.

1 Cubic Centimètre = 17 English Minims.

A Litre of water *weighs* a Kilogramme, or something less than 2¼ Pounds Avoirdupois. A Cubic Centimètre of water *weighs* a Gramme.

French Measures of Length.

1 Mètre = 10 Decimètres = 100 Centimètres = 1000 Millimètres = 39·37079 English inches.

A metre is equivalent to the ten-millionth part of the arc of the meridian, extending from the Equator to the Pole.

Twaddell's Hydrometer.

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
1	1·005	11	1·055	20	1·100
2	1·010	12	1·060	21	1·105
3	1·015	13	1·065	22	1·110
4	1·020	14	1·070	23	1·115
5	1·025	15	1·075	24	1·120
6	1·030	16	1·080	25	1·125
7	1·035	17	1·085	26	1·130
8	1·040	18	1·090	27	1·135
9	1·045	19	1·095	28	1·140
10	1·050				

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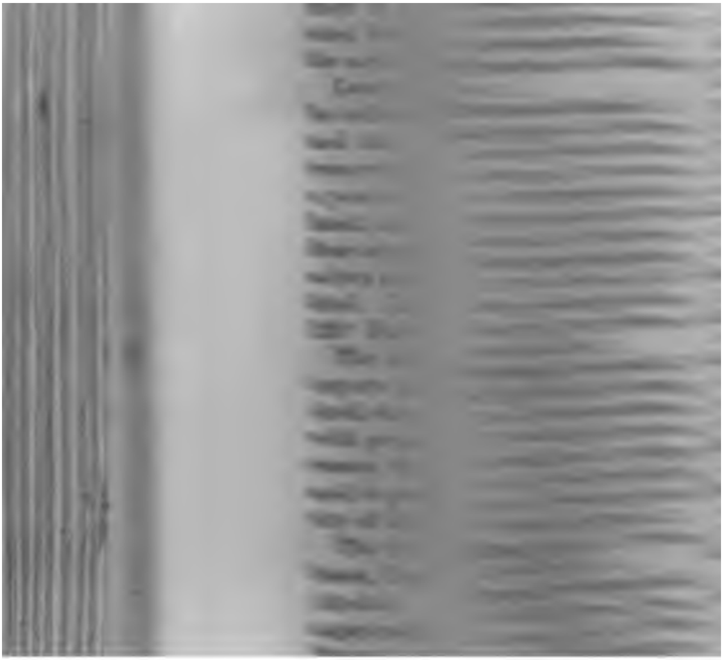

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